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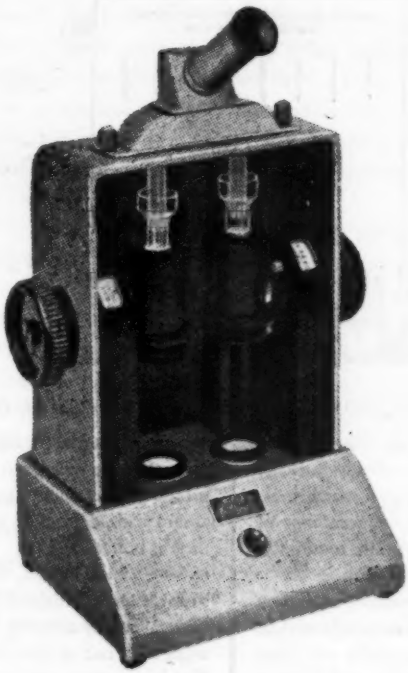

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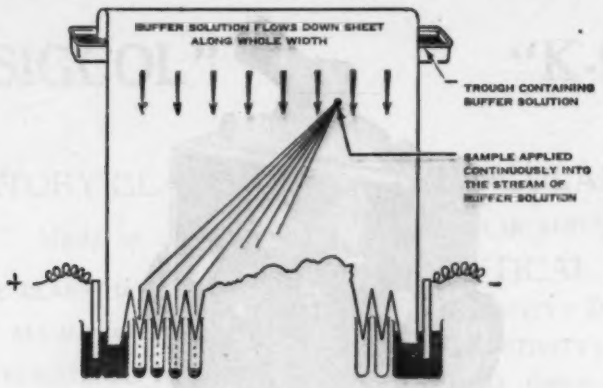
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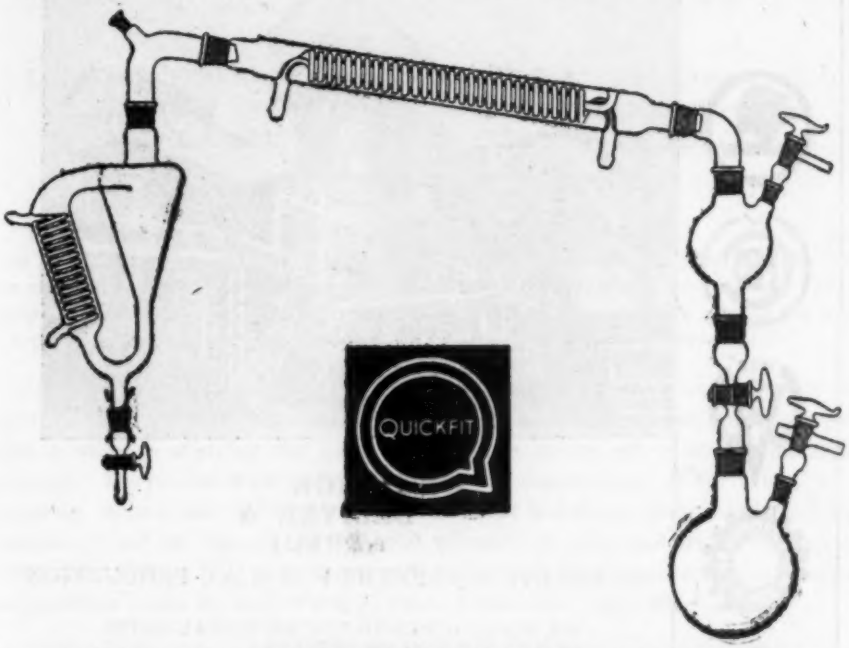

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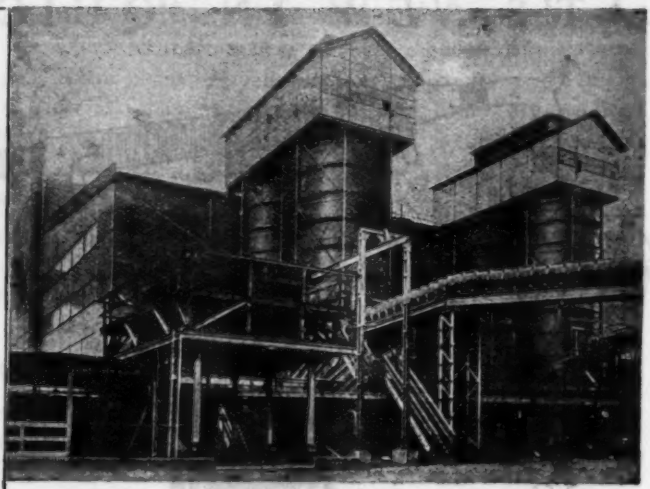

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[Jour. Indian Chem. Soc., Vol. 34, No. 8, 1957]

LIGHT SCATTERING IN SOAP-SOLVENT SYSTEMS. PART I. SODIUM STEARATE IN GLYCERINE AND IN ETHYLENEGLYCOL : DEPOLARISATION AND INTENSITY MEASUREMENTS

By B. G. Naik and K. B. Deshpande

The measurements of depolarisation factors and intensity of light scattered at different directions from gel-forming systems of sodium stearate in glycerine and in ethyleneglycol have shown that the size and anisotropy of the particles decrease during cooling. The gels of higher concentrations contain larger number of particles of slightly larger size than those of lower ones. An attempt has been made to explain the results on the consideration of the behaviour of soap in polar solvents.

Several investigators have measured the depolarisation factors and intensity of the light scattered in different directions from gel-forming systems of soaps in organic solvents with a view to studying the nature of particles in the system and the mechanism of gelation. The present investigation deals with the measurements of the values of depolarisation factors and intensity of light scattered in different directions by gel-forming systems of sodium stearate in two polar solvents, glycerine and ethyleneglycol, during their cooling from a high temperature as these solvents are known to possess pronounced co-dissolving power for soap (Palit, *J. Amer. Chem. Soc.*, 1947, **69**, 3120).

Experimental

Gel-forming Systems.—Gel-forming systems containing different amounts of sodium stearate in glycerine and in ethyleneglycol were prepared in pyrex glass test tubes of internal diameter 1.5" by the usual method (Prasad and Hattiangdi, *Proc. Ind. Acad. Sci.*, 1945, **21A**, 1). The test tube was heated in an oil-bath maintained at 120° and when the contents of the test tube reached the temperature of the bath, it was transferred to the observation bath for depolarisation measurements.

Depolarisation Measurements.—The experimental arrangement and procedure adopted for the depolarisation measurements were the same as used by Sundaram (*ibid.*, 1954, **40A**, 176). The depolarisation factors of the light scattered at 45° (forward), 67°, 90°, 112° and 135° to the direction of the incident beam were measured, taking all the necessary precautions to minimise errors involved in the measurements.

Light Intensity Measurements.—The experimental arrangement for the measurement of intensity was the same as the one used by Sundaram and Desai (*Proc. Nat. Inst. Sci., India*, 1954, **20**, 597), except that the observation bath, which was maintained at 120°, contained Nujol, instead of distilled water. The test tube containing the gel-forming sytem at 120° was placed in the observation bath and the intensities of light scattered at different angles were measured at intervals of 10° till the system cooled down to room temperature. The cooling of the system was effected at an average rate of 1° for every two minutes.

Measurement of the Gelation Temperatures.—Flemming's method was used for the determination of temperature of gelation in the usual manner (Flemming, *Z. physikal. Chem.*, 1902, **41**, 427; Deshpande and Buch, this *Journal*, 1956, **33**, 321).

The results obtained show that the variations in the depolarisation factors and the intensity of scattered light, at different temperatures, are of the same nature for different concentrations of the soap. Fig. 1 shows the curves obtained by plotting the depolarisation factors ρ_u and ρ_h, for the transversely scattered light, against temperature and Fig. 2 shows the curves obtained by plotting the values of the intensity of transversely scattered light and the values of the dissymmetry ratio (I_{45}/I_{135}) against temperature, for the system containing 3% soap (temperature of gelation = 32°).

FIG. 1

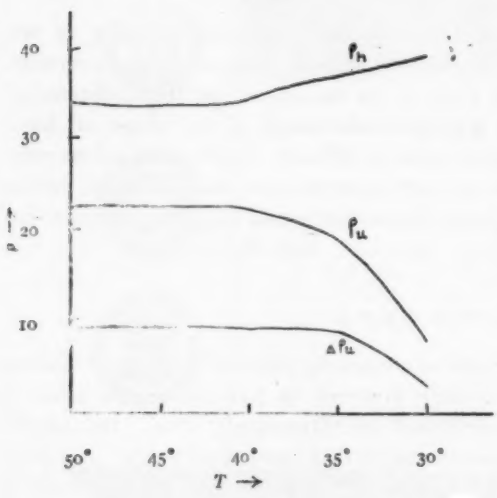
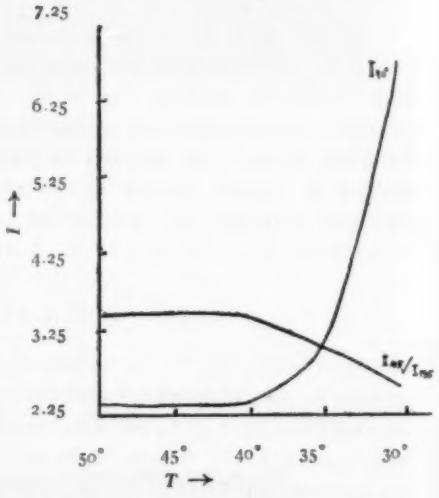


FIG. 2



DISCUSSION

Depolarisation Measurements.—It can be seen from Fig. 1 that no changes take place in the values of ρ_v, ρ_h and ρ_u for the transversely scattered light during cooling until a temperature, a few degrees higher than the gelation temperature, is reached. The values of ρ_v, which are initially low, decrease on further cooling, and again become nearly constant at room temperature. This indicates that the particles are initially slightly anisotropic in nature and that the anisotropy decreases during gelation. There is a slight increase in the values of ρ_h during the last stages of gelation. According to Krishnan (*Proc. Ind. Acad. Sci.*, 1935, **1A**, 717, 782) ρ_h depends on both size and anisotropy. Thus, it seems that simultaneous changes in the size and anisotropy of the particles are taking place during the cooling of the systems, and they are of such a magnitude that no large changes in the values of ρ_h are brought about.

The values of ρ_u, which are initially constant, decrease during the later stages of cooling and become constant at about room temperature. Sivarajan (*Curr. Sci.*, 1951,

20, 202) has stated that when the value of ρ_h is nearly unity, the values of ρ_u can be split up into the anisotropic part and the size part as follows: Contribution due to anisotropy $= 2\rho_v/1+\rho_v$; contribution due to size $= \Delta\rho_u = \rho_u - 2\rho_v/1+\rho_v$.

At the other values of ρ_h, these relations give only approximate indications of the size and the anisotropy effects. The values of $\Delta\rho_u$ have been calculated at different stages of cooling and plotted against temperature (Fig. 1). It is found that the values of $\Delta\rho_u$ remain constant during the cooling of the systems until a temperature, a few degrees above the gelation temperature, is reached. Below this temperature the values decrease during gelation and become constant at room temperature. This shows that the size of the particles decreases during the cooling and consequent gelation of these systems.

The relations put forward by Ganeshan (*Phys. Rev.*, 1924, **23**, 63) and Guinand and Tounelat (*Compt. rend.*, 1947, **225**, 1029) connecting the depolarisation value with the angle of scattering, are not found to be applicable to the systems studied.

Intensity Measurements.—It can be seen from Fig. 2 that the intensity of light scattered by the systems remains constant up to about 60° and then increases continuously during the setting of the systems to gels. This indicates that the particles in these systems increase in number and/or size during gelation. The measurements of the depolarisation factors have, however, shown that the size and anisotropy of the particles decrease during gelation. Hence, it can be concluded that the observed increase in the values of intensity is probably due to an increase in the number of scattering particles.

Angular Variation of Intensity.—From theoretical considerations Mie (*Ann. Physik*, 1908, **25**, 377), Shoulejkim (*Phil. Mag.*, 1908, **48**, 307), Blumer (*Z. Phisik*, 1925, **32**, 112 ; 1926, **38**, 304, 920) and Krishnan (*Proc. Ind. Acad. Sci.*, 1934, **1A**, 147) have shown that with large particles the intensity of the light scattered in the forward direction is greater than that in the backward direction. Their results lead to the conclusion that an increase in the ratio I_{45}/I_{135} indicates an increase in the size of the particles. The values of this ratio at various stages of cooling of the systems studied in this investigation have been plotted against temperature (Fig. 2). These values remain constant up to a certain temperature, beyond which they decrease during the cooling and gelation of the systems, indicating thereby that the size of particles is comparatively large in the initial stages and decreases during cooling and gelation. This conclusion supports the deductions made from the values of ρ_h and $\Delta\rho_u$.

Oster ("Progress in Biophysics and Biophysical Chemistry", Butterworth Springer Ltd., London, 1950, Vol. I, p. 80) has shown that in a system containing very large independent particles, the values of the ratio I_{45}/I_{135} increase with increase in particle size and approach the maximum value of 2.44 in the case of rod-like particles, and 5.98 in the case of disc-like particles, whereas for spherical particles, this ratio increases very rapidly with increase in the size of the particles. In the present investigation the maximum values found for the ratio lie between 3 and 3.4, indicating that the particles in these systems are likely to be in the form of coils or rods.

Effect of Concentration on Intensity.—It is observed that the increase in the concentration of the gel-forming substance in both systems causes an increase in the intensity

of the scattered light as well as in the dissymmetry ratio. However, the increase in the intensity and the dissymmetry ratio is not as large as the increase in the amount of the disperse phase in the gel-forming solution owing to the increase in the concentration. Hence, it is probable that gels of higher concentrations contain a larger number of particles of a slightly larger size than gels of lower concentrations.

From the above study, the following conclusions have been drawn regarding the changes in shape and size of particles in the two systems:

(*i*) The size of the particles decreases during cooling and gelation.

(*ii*) The scattering particles increase in number.

(*iii*) The particles at first join together to form coils.

(*iv*) A gel of higher concentration contains larger number of particles of slightly larger size than a gel of lower concentration.

These conclusions suggest the following mechanism for formation of the gels studied. The soap on mixing with the solvent forms initially a dispersion which is molecular only to a small extent and consisting chiefly of independent colloidal micelles. On cooling the system, reduction in thermal agitation and the nature of the soap-solvent molecules give rise to the possibility of a combination of the two in two different ways, namely (1) the hydrocarbon tail of the soap attracts the hydrocarbon part of the alcohol as in the case of soap-water system, and (2) the polar part of the soap is oriented towards the solvent. Cooling also throws out some of the soap which may be in the molecular solution, thus increasing the number of particles. During the process of aggregation the particles change in shape as indicated by the chan es in ρ_v values. The change is such that the particles decrease in size. The apparent contradiction of particles aggregating to give finally a particle of decreased size can be explained by the consideration that by size is meant the largest dimension occurring in the particle (length in the case of rods, diameter in the case of spheres, etc.) and not its volume. It would then be possible for the particles to form larger ones (with larger volume) and still their size may decrease owing to a change from the non-spherical (rod or coil) to a spherical shape, as the sphere has larger volume for the same dimension. This argument is supported by the fact that the final particles are more isotropic than the initial ones.

The authors are grateful to Dr. Mata Prasad, D.Sc., F.R.I.C., F.N.I., for his keen interest in the progress of the work.

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MAGNETIC STUDY OF METAL DERIVATIVES OF 1 : 3-β-DIKETONE. PART II

By Sagar Mehta and D. M. Desai

The diamagnetic susceptibilities of seven metal chelates of benzoylacetone, namely, Be, Mg, Zn, Cd, Ca, Sr and Ba, have been determined by a modified form of Gouy's balance. The results show the absence of singlet structure in these chelates as all the compounds studied are found to be diamagnetic. The fair agreement between the observed and the calculated values of molar susceptibilities of these chelates, with the exception of cadmium, suggests that in these chelates there is no systematic and appreciable diamagnetic contribution of metal chelate bonds. The replacement of CH_3 group by C_6H_5 group has no abnormal effect on the diamagnetism of these compounds.

In continuation of the work reported earlier (this *Journal*, 1957, **34**, 189) the diamagnetic susceptibility of metal derivatives of benzoylacetone of the second group metals has been studied in this investigation. It appears from the literature that the magnetic study of not a single metal derivative of benzoylacetone has been reported so far.

Experimental

The metal chelates of benzoylacetone, namely Be, Mg, Zn, Cd, Hg, Ca, Sr and Ba benzoylacetonates, were prepared by the known methods using benzoylacetone of Merck's quality and inorganic salts of very high purity. Benzoylacetone was twice distilled in a glass-joint apparatus before use. The compounds so prepared were carefully purified by repeated crystallisations and dried before measurement. The purity of the compounds was determined by the melting point and the metal content, by chemical analysis.

The diamagnetic susceptibilities of these compounds were determined by a modified form of Gouy's balance and the susceptibility values were calculated by using the equation (cf. Angus and Tilston, *Trans. Faraday Soc.*, 1947, **53**, 235),

$$\chi = \frac{\alpha F + C}{w},$$

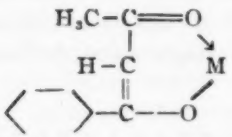
as described previously (*loc. cit.*). The results of these measurements are shown in Table I in which χ_s represents the specific susceptibility values and χ, their molar susceptibilities. The susceptibility values recorded in the table are the mean of at least three independent determinations and these have been expressed in terms of -1×10^{-6} c.g.s. units.

TABLE I

Benzoyl acetonates.	M. W.	χ_a.	χ_M	
			Obs.	Calc.
Be	331.36	0.556	184.20	183.01
Mg	346.66	0.555	192.40	185.55
Zn	387.72	0.511	198.10	198.11
Cd	434.75	0.460	200.00	216.60
Hg*	...	...	...	...
Ca	362.42	0.525	190.30	193.08
Sr	409.97	0.495	203.20	202.85
Ba	459.70	0.451	207.30	214.25

* This compound was found to decompose during the preparation.

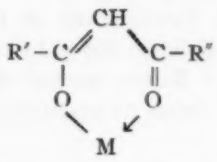
Structure of Metal Benzoylacetonates.—All the compounds studied in this investigation were found to be diamagnetic. Although the theory of singlet structure has been discarded for normal and stable compounds, yet it may be inferred from the magnetic study of these metal chelates, that they do not have a singlet structure as suggested by Sudgen (*J. Chem. Soc.*, 1929, 318) because if these chelates had single electron linkages, they would have shown an overwhelming paramagnetism. The structure of these metal chelates of benzoylacetone like that of the metal chelates of acetylacetone is therefore represented as one involving single and double bonds in the following manner.



Comparison of Molar Susceptibilities.—The molar susceptibilities of these metal chelates have been calculated by using the susceptibility value of benzoylacetonate ion and Angus' values (*Proc. Roy. Soc.*, 1932, **136A**, 569) of metal ions. The susceptibility value of benzoylacetonate ion has been computed in a similar manner (cf. acetylacetonate ion) by making use of Pascal's constants (cf. Bhatnagar and Mathur, "Principles and Application of Magnetochemistry", p. 138) for various atoms and constitutive correction constants and has been found to be -91.33×10^{-6}. The observed and the calculated values of the molar susceptibilities are recorded for the purpose of comparison in the last two columns of Table I.

It is seen that the observed values of molar susceptibility of all the metal chelates of benzoylacetone, except that of cadmium, agree fairly well with those calculated by using Angus' values of metal ions ; a slight departure from the observed values is, however, expected as Angus' values for metal ions used in the calculation are for free ions. The fair agreement between the observed and the calculated values of molar susceptibilities, except in the case of cadmium, would indicate that there is no systematic and appreciable diamagnetic contribution due to metal chelate bonds in these complexes. These results apparently support the observation made in the previous investigation (*loc. cit.*) and are also in agreement with the conclusion reached by Hutchisson and Elliott (*J. Chem. Phys.*, 1948, **16**, 920) in the study of thorium acetylacetonate.

Effect of Chelating Group on M−O *Bonds.*—The structure of metal chelates of acetylacetone and benzoylacetone may, in general, be represented as shown below :



(where M is the metal ion)

In the case of acetylacetonates the two groups R′ and R″ are the same (R′ and R″ = Me) while in the benzoylacetonates the two groups R′ and R″ are different (R′ = Me and R″ = Ph). It is interesting to find out whether the M−O bonds in both acetylacetonate and benzoylacetonate are of the same character or there is any deformation in the case of benzoylacetonate, where there is no symmetry and where the two groups R′ and R″ are different, that is, on one side there is a Me group and on the other there is a phenyl ring.

The computed values for the benzoylacetonate ion and acetylacetonate ion are 91.33 and 50.95 respectively. Hence, the difference between the susceptibility of the two radicals comes out to be 40.38 which corresponds to the diamagnetic contribution of C_5H_2. Similarly, the difference between the benzoylacetonate and acetylacetonate of a particular metal chelate was found out and the average diamagnetic contribution for C_5H_2 group was obtained. This is shown in Table II.

TABLE II

Metal.	χ_M values		Difference.
	Acetylacetonate.	Benzoylacetonate.	C_5H_2
Be	107.5	184.2	76.7
Mg	106.3	192.4	86.1
Zn	121.6	198.1	76.5
Cd	121.4	200.0	78.6
Ca	113.2	190.3	77.1
Sr	127.7	203.2	75.5
Ba	130.9	207.3	76.4
		Average	78.13

It is seen from the above table that except in the case of Mg, there is a close agreement in the difference obtained between the two sets of values. The average difference

which corresponds to the diamagnetic contribution of C_5H_2 comes out to be 39.06 which is in fair agreement with the value obtained from the computed values of the two radicals. These results indicate that in such compounds the replacement of CH_3 group by C_6H_5 group has no abnormal effect on the diamagnetism of these compounds. This conclusion is supported by the work of Kohavec and Kohlrausch (*Ber.*, 1940, **73B**, 1304) who have observed from the study of the Raman spectra of several such compounds that in these chelates the two M−O bonds are practically identical, even when R′ and R″ are different.

The authors wish to express their sincere thanks to Dr. C. R. Kanekar for keen interest and helpful suggestions in this investigation and to Dr. L. N. Mulay who initiated this work.

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AMINO DERIVATIVES OF FERROUS IODIDE

By Sarju Prasad and D. R. Krishnamurty

The amino derivatives of ferrous iodide have been prepared by the action of ferrous iodide on some mono, di, secondary and tertiary amines, their properties studied and structures discussed.

The co-ordination number of iron is six, but compounds in which iron has co-ordination number less than six have also been reported in literature. Reinosuke Hara (*Chem. Abs.*, 1952, 2437[a]) studied the formation of complex salts of α- and β-naphthylamine and *m*- and *p*-tolidine with ferrous sulphate. They gave inflections at approximately 1:1 and 1:2. Breuil (*Compt. rend.*, 1933, **196**, 2009) prepared complex compounds of ferrous chloride and ethylendediamine, but in spite of the chelation, these were not very stable, and decomposed in air. Some double salts such as $FeI_2.2HgI_2.6H_2O$ are reported in literature, but there is no evidence to show that these contain complex ferrous ions.

The present investigation was undertaken with a view to studying the formation of compounds by treating ferrous iodide with aromatic and aliphatic amines in ether.

Experimental

The amine and ferrous iodide used were of B.D.H. "extra pure" quality and ether was distilled over metallic sodium.

General Method of Preparation.—A dilute ethereal solution of the amine was added to the ferrous iodide solution in ether with constant shaking till the precipitation was complete. The precipitate was filtered and washed with anhydrous ether till the washing did not produce any precipitate with ferrous iodide. It was dried at the room temperature, analysed and its properties studied. Iodine was estimated as AgI and iron as Fe_2O_3. Two sets of experiments were carried out simultaneously. The results reported in Tables I, II and III are the average of the two values.

TABLE I

Compounds of ferrous iodide with primary amines.

Amine.	Compounds formed.	Colour.	M.P.*	% Iron.		% Iodine.		% Org. substance (by diff.).	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
p-Toluidine	Di-*p*-toluidino-FI $Fe(Me.C_6H_4.NH_2)_2I_2$	Dark brown	150°	10.60	10.66	48.12	48.45	41.28	40.86
α-Naphthylamine	Di-α-naphthylamino-FI $Fe(C_{10}H_7.NH_2)_2I_2$	Light brown	165°	9.52	9.37	43.10	42.58	47.38	47.05
β-Naphthylamine	Di-β-naphthylamino-FI $Fe(C_{10}H_7.NH_2)_2I_2$	Black	147°	9.62	9.37	42.72	42.58	47.66	47.05
Xylidine	Di-xylidine-FI $Fe(Me_2.C_6H_3NH_2)_2I_2$	Yellowish brown	215°	9.97	10.12	45.22	45.57	44.81	43.91
Aniline	Di-anilino-FI $Fe(C_6H_5NH_2)_2I_2$	Dark brown	140°	11.22	11.26	51.80	51.17	36.98	37.57
p-Phenetidine	Di-*p*-phenetidino-FI $Fe(C_2H_5O.C_6H_4NH_2)_2I_2$	Grey	220°	9.54	9.56	43.36	43.45	47.10	46.99
m-Toluidine	Di-*m*-toluidino-FI $Fe(CH_3.C_6H_4.NH_2)_2I_2$	Muddy	197°	10.23	10.66	47.52	48.45	42.25	40.89
p-Aminodiethyl-aniline	Di-*p*-aminodiethylanilino-FI $Fe(NH_2.C_6H_4.NEt_2)_2I_2$	Black	210°	8.44	8.75	40.10	39.77	51.46	51.48
o-Toluidine	Di-*o*-toluidino-FI $Fe(Me.C_6H_4.NH_2)_2I_2$	Black	183°	11.23	10.66	46.96	48.45	41.80	40.89
Benzylamine	Dibenzylamino-FI $Fe(C_6H_5.CH_2.NH_2)_2I_2$	Brown	230°	11.35	10.65	47.98	48.43	40.67	40.92
o-Anisidine	Di-*o*-anisidino-FI $Fe(CH_3O.C_6H_4.NH_2)_2I_2$	Brown	228°	10.71	10.04	45.24	45.63	44.06	44.33
o-Phenetidine	Di-*o*-phenetidino-FI $Fe(C_2H_5O.C_6H_4NH_2)_2I_2$	Orange-brown	189°	9.55	9.56	43.0	43.45	47.45	45.99
p-Anisidine	Di-*p*-anisidino-FI $Fe(CH_3O.C_6H_4.NH_2)_2I_2$	Brown	216°	10.85	10.04	45.82	45.63	45.33	44.33
*iso*Propylamine	Di-*iso*propylamino-FI $Fe(CH_3.CH_2.CH.NH_2)_2I_2$	Reddish brown	180°	13.12	13.06	59.72	59.34	27.16	27.60

FI denotes ferrous iodide.

* Melts with decomposition.

* Melts with decomposition.

TABLE II

Compounds of ferrous iodide with primary diamines.

Diamine.	Compound formed.	Colour.	*M.P.	% Iron.		% Iodine.		% Org. substance (by diff.).	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
o-Naphthalenediamine	*o*-Naphthalenediamino-FI $Fe[C_{10}H_6(NH_2)_2]I_2$	Black	140°	12.12	11.94	54.52	54.26	33.36	33.80
Dianisidine	Dianisidino-FI $Fe(CH_3O.NH_2.C_2H_3)_2I_2$	Green	276°	10.91	10.54	48.92	47.88	40.17	41.58
Ethylenediamine	Ethylenediamino-FI $Fe(NH_2.CH_2.CH_2NH_2)I_2$	Dark brown	118°	15.21	15.10	67.20	68.63	17.59	16.37
p-Phenylenediamine	*p*-Phenylenediamino-FI $Fe[C_6H_4(NH_2)_2]I_2$	Black	210°	12.80	13.37	61.40	60.75	25.30	25.88
o-Tolidine	*o*-Tolidino-FI $Fe(CH_3.NH_2.C_6H_3)_2I_2$	Ash colour	206°	11.20	10.70	47.95	48.62	40.85	40.68
o-Phenylenediamine	*o*-Phenylenediamino-FI $Fe[(NH_2)_2.C_6H_4]I_2$	Black	225°	13.81	13.37	60.21	60.75	26.98	25.88
Phenylhydrazine	Phenylhydrazino-FI $Fe(C_6H_5.NH.NH_2)I_2$	White	155°	13.04	13.37	61.20	60.75	25.76	25.88
Benzidine	Benzidino-FI $Fe(C_6H_4.NH_2)_2I_2$	Yellowish brown	219°	11.31	11.32	51.26	51.41	37.43	37.26

* Melts with decomposition.

TABLE III

Compounds of ferrous iodide with secondary and tertiary amines.

Amine.	Compound formed.	Colour.	M.P.	% Iron.		% Io line.		% Org substance (by diff.).	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
Diphenylamine	Tri-diphenylamino-FI $Fe[(C_6H_5)_2.NH]_3I_2$	Brown	224°	7.08	6.83	31.60	31.06	61.32	62.11
Benzylaniline	Tribenzylanilino-FI $Fe(C_6H_5.NH.CH_2.C_5H_5)_3I_2$	Yellowish brown	256°	6.50	6.50	28.76	29.53	64.74	63.97
Ethylaniline	Triethylanilino-FI $Fe(C_6H_5.NH.C_2H_5)_3I_2$	Black	213°	8.42	8.29	37.92	37.70	53.66	54.01
Di-*p*-tolylamine	Tri-di-*p*-tolylamino-FI $Fe[(CH_3.C_6H_4)_2NH]_3I_2$	Yellowish brown	222°	6.27	6.20	28.08	28.16	65.65	65.64
Dibenzylamine	Tri-dibenzylamino-FI $Fe[(C_6H_5.CH_2)_2NH]_3I_2$	Brown	214°	5.80	6.20	28.32	28.16	65.88	65.64
Di-*n*-propylaniline	Tri-di-*n*-propylanilino-FI $Fe[(CH_3.CH_2.CH_2)_2NH]_3I_2$	Yellowish brown	263°	9.32	9.11	42.57	41.39	48 11	49.49
n-Propylaniline	Tri-*n*-propylanilino-FI $Fe[(C_6H_5.NH.CH_2.CH_3)]_3I_2$	Do	239°	7.76	7.81	35.52	35.49	56.72	56.70
Tribenzylaniline	Tri-tribenzylamino-FI $Fe[(C_6H_5.CH_2)_3N]_3I_2$	Brownish black	264°	4.74	4.70	21.65	21.56	73.61	73.74
Triethylamine	Tri-triethylamino-FI $Fe[(C_2H_5)_2N]_3I_2$	Brown	215°	9.23	9 10	41.26	41.39	49.51	49 51
Dimethyl-*o*-toluidine	Tri-dimethyl-*o*-toluidino-FI $Fe[CH_3.C_6H_4.N(CH_3)]_3I_2$	Yellowish brown	211°	7.83	7.81	31.98	32.50	60.19	59.69

Discussion

The co-ordination number of iron in the cases studied is either two or three and therefore the effective atomic number does not assume the inert gas configuration. The compounds are stable in the dry atmosphere at room temperature, but begin to hydrolyse slowly as soon as they come in contact with moisture or when treated with sodium carbonate or sodium hydroxide solutions. The compounds formed with mono-amines hydrolyse slowly at the room temperature and rapidly at higher temperatures and ferrous hydroxide is precipitated according to the following equations:

$$Fe\ (2\ Am.)\ I_2 + 2H_2O \rightarrow Fe(OH)_2 + 2\ Am.\ HI$$
$$Fe\ (2\ Am.)\ I_2 + 2NaOH \rightarrow Fe(OH)_2 + 2NaI + 2\ Am.$$

but those obtained with the diamines are more stable and hydrolyse slowly even on boiling.

On heating alone, these decompose, giving out iodine which condenses on the cooler parts of the tube. When they are heated with soda-lime, the corresponding amines separate out and condense on the cooler parts of the tube. All the compounds respond to the diazo test.

It appears that the amines attach themselves to the central atom, chelate compounds being formed in the case of diamines, which is responsible for the greater stability of these compounds. In the case of secondary and tertiary amines, three molecules are attached to the central atom.

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USE OF THIOSEMICARBAZONES AS REAGENTS IN INORGANIC ANALYSIS

By P. N. Bhargava and M. J. Rao

Thiosemicarbazones of six aldehydes and ketones have been tested as reagents for the common inorganic cations at different p_H ranges and the resulting colour changes, formation of precipitates as well as the solubilities of the precipitated complexes noted. Precipitates are formed with Ag^+, Hg^{2+} and Cu^{2+} in all cases and in some cases with Co^{2+} and Ni^{2+}, but with Ba^{2+} and Mg^{2+} in one case only. The thiosemicarbazones of *p*-hydroxybenzophenone, piperonal and benzoin have been found good for the quantitative estimation of Cu^{2+} and those of piperonal and veratraldehyde, to furnish quantitative precipitates with Hg^{2+}. Veratral and *m*-hydroxybenzylidene derivatives have been found to be highly sensitive for Cu^{2+} and Ni^{2+} even at 1:10 dilutions. Some of the thiosemicarbazones also exhibited colorations with some anions as ferricyanide, ferrocyanide, nitrite, molybdate, chromate, thiocyanate, borate, tungstate and thiosulphate.

Neuberg and Neiman (*Ber.*, 1902, **35**, 2049) first found that the thiosemicarbazones of a few aldehydes and ketones could be used for identifying Ag, Hg and Cu as they afforded sparingly soluble derivatives with these metals in solution due to formation of complexes. This investigation was therefore taken up in order to determine the range of such complex formation under properly controlled conditions and also their solubilities and stabilities as well as their use in quantitative estimations of metals.

Experimental

The thiosemicarbazones of six aldehydes and ketones were prepared by the methods of Neuberg and Neiman (*loc. cit.*) and Scott *et al.* (*J. Amer. Chem. Soc.*, 1945, **67**, 1767). All the compounds are new except *p*-aminoacetophenone thiosemicarbazone which has been prepared according to the method of Guha Sircar and Satpathy (this *Journal*, 1954, **31**, 550), Mitra and Guha Sircar (*ibid.*, 1955, **32**, 433) and Indian Patent (1950, 43527).

The melting points and the analytical data of the thiosemicarbazones are recorded in Table I.

Table I

	Aldehydes or ketones.	M.P.	% Sulphur. Found.	Calc.
1.	*p*-Hydroxybenzophenone	186°	11.71	11.82
2.	Piperonal	185°	15.38	15.46
3.	Veratraldehyde	200°	14.26	14.35
4.	*m*-Hydroxybenzaldehyde	173°	16.36	16.41
5.	*p*-Aminoacetophenone	178°	15.52	15.39
6.	Benzoin	174°	11.13	11.23

An 1% solution of the reagent in rectified spirit was added dropwise to 10 drops of each of 2*N* solutions of salts of metals arranged in their analytical order (Ag, Hg, Pb, Cu, Cd, Bi, As, Sb, Sn, Fe, Al, Cr, Co, Ni, Zn, Mn, Ca, Sr, Ba, Mg) in a series of test tubes containing 2 c.c. of an acetate buffer solution of p_H between 3.42 and 5.89. The formation of any precipitate or colour change in the mixture was noted both in cold and on heating. When the precipitate was formed, its precipitation was completed by further addition of the reagent and warming the mixture on the water-bath. The precipitate was filtered, washed and the filtrate tested for the respective cation by further addition of the reagent solution. The p_H ranges suitable for coagulation of precipitates were noted and the precipitation was taken to be quantitative. The complexes were further washed with alcohol to free them of the reagent and their solubilities in dilute HCl, ammonia, acetone, alcohol and chloroform were qualitatively studied. The complexes were also decomposed by strong mineral acids and the liberated cations were tested by some standard reagents for ascertaining the actual formation of the complex.

Reactions of the Reagents with the Cations at Different p_H (3.42-5.89)

p-Hydroxybenzophenone thiosemicarbazone formed yellow precipitate with Ag^+, Hg^{2+}, the silver complex first turning brown and finally black in light. Ni^{2+} gave a white precipitate, changing to buff and Co^{2+} gave a deep red colour on standing. Cu^{2+} formed a green precipitate, turning black on heating and was quantitative, soluble in mineral acids but insoluble in ammonia, acetone, chloroform, alcohol and water.

Piperonal thiosemicarbazone gave a yellow precipitate with Ag^+, Hg^{2+}, Ni^{2+}, white with Ba^{2+} and Mg^{2+} and a green precipitate with Cu^{2+}. The Cu^{2+} and Hg^{2+} precipitates were quantitative, soluble in mineral acids but insoluble in ammonia, acetone, chloroform and alcohol.

Veratraldehyde thiosemicarbazone gave a yellow gel with Ag^+ and Hg^{2+}, turning black and green respectively on heating. Cu^{2+} formed a green precipitate. Hg^{2+} complex was quantitative and soluble in strong mineral acids, insoluble in dilute acids, dilute ammonia and alcohol.

m-Hydroxybenzylidene thiosemicarbazone formed a white precipitate with Ag^+ and Hg^{2+}, green with Cu^{2+} and chocolate with Co^{2+}. Ni^{2+} gave a red colour on standing. The Ag^+ precipitate was quantitative, soluble in dilute HNO_3 but sparingly soluble in alcohol and water.

p-Aminoacetophenone thiosemicarbazone gave a yellow precipitate with Ag^+ and Hg^{2+}, the silver complex turning black in light. The precipitates were not quantitative.

Benzoin thiosemicarbazone gave a yellow precipitate with Ag^+ and Hg^{2+}, the silver complex turning black in light. The precipitate with Cu^{2+} was bluish green, quantitative, soluble in mineral acids but insoluble in ammonia, alcohol, acetone, chloroform and water.

The reactions of the anions in neutral as well as in acid media were studied. The anions tested were ferricyanide, ferrocyanide, nitrite, molybdate, chromate, tungstate,

thiocyanate, thiosulphate and borate. To about 3 c.c. of the anion solution 5 drops of an 1% solution of the reagent in rectified spirit were slowly added and the colour changes were noted both in the cold and on warming. In case of ferricyanide, ferrocyanide, chromate and nitrite, two sets of solutions were used. To one set 5 drops of glacial acetic acid and 5 drops of the reagent solution were added and to the other set only 5 drops of acetic acid were added. The changes in coloration, whether immediate or delayed, were observed.

Colour Changes with the Reagents in Neutral and Acidic Media with Anions

p-Hydroxybenzophenone thiosemicarbazone produced colour changes in acidic medium with ferricyanide, ferrocyanide, nitrite, molybdate chromate and thiocyanate, the colour being respectively green, yellow, blue, bluish green and red. In neutral medium it gave a yellow colour with chromate.

Piperonal thiosemicarbazone produced a bluish green coloration with ferrocyanide, molybdate and chromate and a red colour with thiocyanate in acid medium. In neutral medium it gave a yellow precipitate with ferrocyanide.

Veratraldehyde thiosemicarbazone gave a green coloration with ferricyanide and chromate, a yellow colour with nitrite and a light blue colour with molybdate in acid medium. In neutral medium, it gave a yellow precipitate with ferrocyanide.

m-Hydroxybenzylidene thiosemicarbazone produced a blue colour with ferricyanide, green coloration with ferrocyanide, molybdate and chromate and yellow with nitrite and thiosulphate in acid medium. In neutral medium it gave a yellow precipitate with ferrocyanide.

p-Aminoacetophenone thiosemicarbazone gave a green colour with ferrocyanide and tungstate, yellow with nitrite and blue with molybdate in acid medium.

Benzoin thiosemicarbazone produced green, yellow, blue and blood-red colorations with ferrocyanide, nitrite, molybdate and chromate respectively in acid medium. In neutral medium, it gave a yellow precipitate with ferrocyanide and molybdate.

In the case of coloured complexes different dilutions of the cation solutions were prepared and the sensitivity of the reagents for them was noted both in solution and by spot test on a filter paper. The sensitivity of the reagents towards metallic cations is mentioned in Table II.

TABLE II

(1 g. in c.c.)

Cation.	Serial number of reagents					
	1.	2.	3.	4.	5.	6.
Ag^{+}	10^{5}	10^{6}	10^{7}	10^{4}	10^{5}	10^{5}
Hg^{2+}	10^{5}	10^{4}	10^{4}	10^{3}	10^{5}	10^{4}
Cu^{2+}	10^{5}	10^{5}	10^{4}	10^{5}	10^{4}	10^{5}
Co^{2+}	10^{5}	...	...	10^{5}	...	...
Ni^{2+}	10^{4}	10^{5}	...	10^{7}	...	...

Spot Test.—In case of Hg^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}, a drop of the cationic solution was placed on the filter paper, dried and treated with a drop of an 1% alcoholic solution of the reagent. The spot was then exposed to ammonia vapour.

Quantitative Estimations

Quantitative estimations could not be made with Ag, Ni and Co complexes as they were very unstable and liable to decomposition on drying. Cu^{2+} and Hg^{2+} were estimated quantitatively.

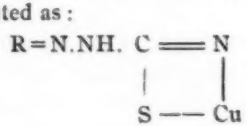
Estimation of Cu^{2+}.—The standard solution (10 c.c.) was taken in a beaker and after addition of an acetate buffer (100 c.c.) of p_H 4.99 was heated to 50°-60°. A hot 1 or 2% solution of the reagent in rectified spirit was added dropwise with constant stirring till complete precipitation. The temperature was maintained at 50°-60° for about ½ hour with occasional stirring. It was allowed to settle for 1 hour and filtered when cold. The precipitate was first washed with hot water and then with 2% alcohol and dried at 100-110° to a constant weight. The results assuming 1 : 1 combination between *p*-hydroxybenzophenone thiosemicarbazone and Cu and 2 : 1 between piperonal or benzoin thiosemicarbazones and Cu are recorded below.

TABLE III

Standard soln. taken = 10 c.c.

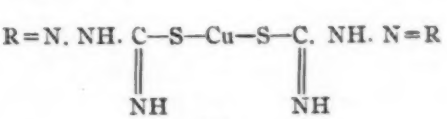
Wt. of the complex.	Reagent No.		
	1.	2.	6.
Mean (g.)	0.1654	0.2564	0 3120
Calc. (g.)	0.1663	0.2588	0 3158

The structures of the complexes of reagents No. 1 (I) and 2 or 3 (II) may be represented as :



(I)

(R = ketonic ligand for reagent No. 1)



(II)

(R = aldehydic or ketonic ligand for reagents No. 2 & 3)

A weighed amount of the copper complex was taken in a weighed porcelain crucible and decomposed by HNO_3 (1 : 1). The acid was evaporated to dryness and the complex ignited to a constant weight. The difference in weight of CuO from the calculated percentage of copper is recorded in Table IV.

TABLE IV

	Reagent No.		
	1.	2.	6.
% Cu (found)	19.31	11.88	9.94
% Cu (calc.)	19.11	12.27	10.07

Estimation of Hg^{2+} *Complex.*—To a standard solution (10 c.c.) of mercury in a beaker an acetate buffer (50 c.c.) at p_H 5.6 was added, followed by 2% alcoholic solution of the reagent dropwise with constant stirring till complete precipitation. The mixture was allowed to settle for 3 to 4 hours, filtered and washed first with slightly warm water and then with 2% alcohol. The rest of the procedure was the same as with Cu complex. With reagent No. 2 mean wt. of the complex found was 0.2128 g. (calc. 0.2108 g.). Mean wt. of the complex with reagent No. 3 found was 0.2204 g. (calc. 0.2188 g.).

The weights of the complexes were slightly high due to the difficulty in removing the reagents by washing. The structure of these complexes corresponds to the structure as mentioned above.

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PHASE BEHAVIOUR OF SODIUM OLEATE IN NUJOL

By K. B. Deshpande and K. P. Buch

The changes in the phases of sodium oleate in different porportions of Nujol at various temperatures have been studied. It is found that the systems show the existence of the following phases: (*i*) isotropic liquid, (*ii*) neat soap, (*iii*) middle soap, (*iv*) waxy soap, (*v*) soap curd and (*vi*) fine soap particles behaving unlike soap crystallites.

The determination of the phase behaviour of soaps in hydrocarbon solvents is of importance in the study of the application of these systems as high-temperature greases. Also the attendant determination of the solubility of the soap in the solvent may prove useful for understanding the phenomenon of gelation occurring in such systems with certain concentrations of the soap. The previous work in this direction includes the study of (*a*) sodium palmitate in some organic solvents (Vold, Legget and McBain, *J. Phys. Chem.*, 1940, **44**, 1058; 1942, **46**, 429), (*b*) sodium and calcium stearates in cetane (Vold *et al.*, *ibid.*, 1946, **50**, 39; *J. Phys. Coll. Chem.*, 1948, **52**, 1424; *J. Amer. Chem. Soc.*, 1951, **73**, 2006), (*c*) lithium stearate and lithium 12-hydroxystearate in some hydrocarbon oils (Evans *et al.*, *J. Appl. Chem.*, 1952, **2**, 252), (*d*) sodium phenylstearate in benzene (Honig and Singleterry, *J. Phys. Chem.*, 1954, **58**, 201), and (*e*) aryl stearate in benzene (Honig *et al.*, *ibid.*, 1956, **60**, 1114). The present investigation deals with the study of the behaviour of sodium oleate in Nujol using the visual method (McBain *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 1970).

Experimental

Materials used were sodium oleate manufactured by B.D H. (containing excess acid = 0.001 equivalent per mol. for the acid recovered from the soap; eq. wt. = 284.5 and I.V. = 88.34.) and Nujol, a product of Messrs Stanco Incorporated, New Jersey, U.S.A. (d = 0.8753; μ = 1.4810 at 30°). The soap was dried to a constant weight at 105°. Requisite amounts of soap and Nujol (total weight about 0.5 g.) were weighed out into a small pyrex glass test tube of length 3″ and diameter 0.4″, with a constriction at a distance of about 1.5″ from the bottom. The tube was then evacuated until air bubbles had ceased to evolve from the system. It was then sealed under vacuum by heating at the constriction. The tubes were then heated in an air-oven made of asbestos cement sheets in the form of a cube of 8″ side. This was heated by two heating coils. The oven had a rotatable iron shaft, running across its length, which carried a circular iron disc (diameter 5.5″) in which were cut six radial slits of 1.5″ × 0.5″. Each slit had two breadth-wise projections, one of which, situated near the centre of the disc, had a hole in it whereas the other served as a groove in which a screw with a concave bottom could be moved. A filled tube could be held in position by inserting its sealed end in the hole in one of the projections and by bringing the concave bottom of the screw in the other projection to press

against the bottom of the tube. The two heating coils were connected in parallel with each other and in series with a variable resistance, an ammeter and a 230 volt D.C. output.

This arrangement allowed six samples to be heated simultaneously. Any one of them could be brought at will against the windows provided in the walls other than those which carried the shaft. These windows were covered with optical glass for observation. The sample could be shaken vigorously, whenever required, by rotating the shaft rapidly. This was necessary to get a macroscopically homogeneous sample for examination. No serious temperature gradients were observed since calibrated thermometers maintained at different levels in the oven, showed the same reading. A 100 c.p. point-o-lite was used as a source of light.

Procedure.—The systems were heated until they completely melted into a homogeneous isotropic liquid and were then cooled to various low temperatures being allowed to remain at each temperature for 3 hours. Visible changes that could be observed with or without the help of nicols were recorded. Particularly, the following changes were observed with a fair accuracy employing, when necessary, slow heating over a narrow range: (*i*) the temperature, T_i, at which an anisotropic material first appeared in the system; (*ii*) the temperature, T_g, at which the system thickened to a consistency high enough to prevent it from flowing when the tube was inverted; (*iii*) the temperature, T_c, at which the system first started forming soap curd. The appearance of the tubes was also observed at various intervals on standing at room temperature and was found to remain essentially unchanged.

The values of T_i, T_g, and T_c in degrees centigrade, determined for various compositions are recorded in Table I in which the compositions (*c*) are expressed in terms of the weight of soap in 100 g. of the system. The appearance of the systems on cooling is briefly described in the last column of Table I.

TABLE I

Transition temperature of sodium oleate-nujol system.

	c.	T_i.	T_s.	T_g.	Changes in appearance.
A	100.00	247°	237°	196°	Homogeneous isotropic liquid (=H.i.l.) gave neat soap which changed to waxy soap and then curd.
B	84.95	228°	216°	190°	
C	76.25	221°	207°	188°	
D	61.27	219°	206°	186°	
E	49.98	217°	178°	196°	H.i.l. gave neat soap & then separated into layers: isotropic liquid at the top and middle soap below; the upper layer became anisotropic and the layers then diffused and soap curd was developed all over the system.
F	39.30	206°	170°	175°	
G	25.32	176°	166°	166°	H.i.l. became viscous and formed a deposit of crystallites; the liquid then became anisotropic and the mass gave a loose gel which developed soap curd.
H	19.96	174°	167°	...	Similar to that in G except that no curd was formed.
I	9.37	174°	172°	...	Same as above except that the gel formed was more rigid.
J	5.09	166°	188°	...	H.i.l. became viscous, set to a clear transparent gel which developed a slight opacity on cooling.
K	2.92	155°	186°	...	
L	0.98	125°	170°	...	

Discussion

Though the method used allows transition temperatures to be determined only within a certain limit of accuracy, these observations suffice to provide a qualitative picture of the phenomena which occur on cooling the soap-solvent systems.

Curves I to III (Fig. 1) show the plots of the various transition temperatures against compositions. If the points representing T_i are joined (curve I), it is observed that the solubility of soap is very low, being only 5% at 165°. It increases rapidly as the temperature is increased. This curve shows three inflections (at 50%, 25% and 10%). This seems to indicate that the anisotropic material which separates out at temperatures below each portion of the curve between two consecutive points of inflection is not of the same type in all cases. This is realised in practice as shown below: (1) Up to the first inflection "neat soap" is formed from the isotropic liquid. ( ) Below the portion of the curve after first inflection, the isotropic liquid does not give neat soap but "middle soap" which is immiscible with isotropic liquid and then neat soap. Again, what separates on solidification from this composition range is not waxy soap, but curds. (3) Below the portion after the second inflection (25%), the isotropic liquid gives a deposit of fine soap particles which give opaque gels. (4) Below the portion after the third inflection (1%), the systems which form transparent isotropic gels at higher temperatures become anisotropic. The curves II and III, obtained by plotting T_g and T^c respectively against temperature, show inflections which can be similarly interpreted.

Phases in the System.—An approximation of the phase boundaries can be made from the curves I, II and III, as shown in Fig. 1. (The vertical lines do not represent a sharp separation of two phases; they are marked only to show approximately the difference in phases on the two sides of the lines). The zones enclosing the various phases are:

A. Homogeneous isotropic liquid or solution occupying a zone above the curve abcde, where d is the intersection point of curves I and II.

B. A zone in which neat soap exists.

C. A zone in which middle soap exists along with neat soap.

D. A zone of soap particles which can form opaque loose gel.

E. A zone of transparent, isotropic gels.

F. A zone in which waxy soap exists.

G. A zone of soap curds which get solvated on cooling.

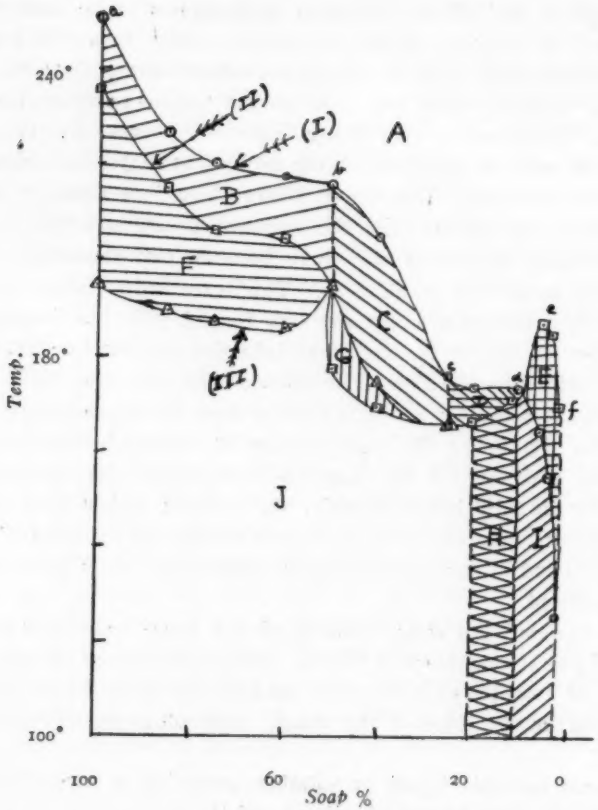
H. A zone of loose opaque gels which show tendency to form curd on standing.

I. A zone of transparent gels which develop slight opacity but do not form curds, even after long standing at the room temperature.

J. A zone in which soap curds develop on cooling and standing into more opaque white soap.

As far as visual observations indicate, the compositions above 25% of the soap show the phenomenon of crystallisation. All these systems ultimately develop soap curds which are known to develop progressively more orderly structure on cooling from a high temeperature.

FIG. 1



The colloidal phenomena are peculiar only to systems containing 25% or less of soap. In these systems, some of which contain particles looking like granules, syneresis is completely absent even after long standing, showing that both the loose and the firm gels are quite stable. Further, no curd formation takes place in the systems. On cooling, their consistency increases and ultimately opaque, white loose gels are formed. The process of the formation of gels, indicative of colloidal behaviour, is essentially dissimilar to crystallisation in which particles grow on cooling, leaving behind a mother-liquor. In the process of gelation, because of coalescence and adsorption, the primary particles grow in size and adsorb the liquid in which they are suspended.

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SPECTROPHOTOMETRIC STUDY OF METAL CHELATES. PART I. ALUMINIUM SULPHOSALICYLATE

By R. K. Nanda and S. Aditya

The dissociation constant of the aluminium sulphosalicylate chelate has been determined at p_H 2.4, at different ionic strengths, by displacement method. The average value at the ionic strength 0.02, 0.05 and 0.2 are 1.72×10^{-3}, 1.94×10^{-3} and 2.58×10^{-3} respectively. The dissociation constant of the ferric sulphosalicylate chelate has also been determined at the same p_H. At ionic strength 0.02, 0.05 and 0.2 the average values are 1.14×10^{-5}, 1.39×10^{-5} and 1.57×10^{-5} respectively. The molar extinction coefficient of ferric sulphosalicylate chelate at 500 mμ has been determined and is 2036.

Aluminium is known to form complexes with many hydroxy-acids. More recently Lasater and Anderson (*J. Amer. Chem. Soc.*, 1952, **74**, 1429) have studied the aluminium sulphosalicylate complex spectrophotometrically by the displacement method. They have used the coloured copper sulphosalicylate complex as the indicator and from the shift obtained in optical density, on adding aluminium perchlorate solution, have determined the molecular composition as also the dissociation constant of the aluminium complex. It is true, as reported by them, that the ferric sulphosalicylate complex cannot be suitably used as indicator for the determination of the molecular composition of the aluminium complex by Job's method, as no appreciable shift is obtained at comparable concentrations of iron and aluminium. But from the dissociation constants reported by Foley and Anderson (*ibid.*, 1948, **70**, 1195) for the ferric sulphosalicylate complex and that for the aluminium complex by Lasater and Anderson (*loc. cit.*), a measurable shift was to be expected, provided that sufficient aluminium ions were present in the system. In the present work the dissociation constant of the aluminium sulphosalicylate complex has been determined, assuming the complex to be of the (1 : 1) type, at different ionic strengths, using iron sulphosalicylate as the indicator, at p_H 2.4. The dissociation constant of the ferric sulphosalicylate complex had also to be determined at different ionic strengths as such data were not available in literature. Incidentally, the extinction coefficient of the ferric complex has also been determined at 500 mμ and at p_H 2.4.

Experimental

Ferric perchlorate solution was prepared by dissolving the reagent grade iron powder in perchloric acid and then oxidising with hydrogen peroxide. The excess hydrogen peroxide was destroyed by heating over a water-bath. Aluminium perchlorate was prepared by adding equivalent amounts of barium perchlorate and aluminium sulphate solutions. Aluminium, in the solution of aluminium perchlorate, thus obtained, was estimated, weighing as oxide. Reagent grade sulphosulicylic acid was used and the stock solution was standardised against a standard NaOH solution.

All measurements of optical densities were taken with a Hilger 'UVISPEK', model H 700/303, spectrophotometer using a quartz prism. Matched glass cells of 10 mm light path were always used. The slit width was always 0.02 mm. Measurements were taken at room temperature ranging between 25° and 30°. In this connection it may be mentioned that Turner and Anderson (*ibid.*, 1949, **71**, 913) measured the optical density of copper sulphosalicylate complex at 22°, 25°, 27° and 30° and reported that the optical densities were within experimental error. So in the present work the optical densities were taken to be independent of temperature, over the range of variation of room temperature. Optical densities were measured at 500 mμ ; p_H measurements were made with a Marconi p_H-meter, model TF 511 D.

TABLE I

1	2	3	4	5	6	7	8	9
Conc. of $NaClO_4$.	Total molar concentration of Fe^{3+}.	Sulphosalicylic acid.	Al^{3+}.	Optical density of the soln.	$K_{red} \times 10^5$.		$K_{Ala} \times 10^3$.	
0.02	0.0002	0.00018	...	0.306	0.98		...	
,,	0.0002	0.00018	0.002	0.276	...		1.54	
,,	0.0002	0.00018	0.004	0.253	...		2.00	
,,	0.00028	0.0002	...	0.365	1.16		...	
,,	0.00028	0.0002	.002	0.337	...	Av 1.14	1.81	Av. 1.72
,,	0.00028	0.0002	0.004	0.315	...		1.78	
,,	0.0004	0.0002	...	0.384	1.27		...	
,,	0.0004	0.0002	0.004	0.347	...		1.59	
,,	0.0004	0.0002	0.006	0.332	...		1.60	
0.05	0.0002	0.00018	...	0.299	1.19		...	
,,	0.0002	0.00018	0.002	0.267	...		2.23	
,,	0.0002	0.00018	0.004	0.246	...		2.22	
,,	0.00028	0.0002	...	0.358	1.43		...	
,,	0.00028	0.0002	0.002	0.325	...		1.67	
,,	0.00028	0.0002	0.004	0.310	...	,, 1.39	2.12	,, 1.94
,,	0.00032	0.0002	...	0.359	1.35		...	
,,	0.00032	0.0002	0.0032	0.327	...		1.76	
,,	0.00032	0.0002	0.0048	0.316	...		1.98	
,,	0.0004	0.0002	...	0.379	1.60		...	
,,	0.0004	0.0002	0.004	0.339	...		1.68	
,,	0.0004	0.0002	0.006	0.326	...		1.82	
0.2	0.0002021	0.0001821	...	0.294	1.51		...	
,,	0.0002021	0.0001821	0.002	0.268	...		2.73	
,,	0.0002021	0.0001821	0.004	0.251	...		2.75	
,,	0.000283	0.0002023	...	0.360	1.57		...	
,,	0.000283	0.0002023	0.002	0.334	...	,, 1.57	2.57	,, 2.58
,,	0.000283	0.0002023	0.004	0.315	...		2.62	
,,	0.0004242	0.0002023	...	0.383	1.63		...	
,,	0.0004042	0.0002023	0.004	0.349	...		2.37	
,,	0.0004042	0.0002023	0.006	0.336	...		2.44	

For the determination of the dissociation constant of the aluminium sulphosalicylate complex, different amounts of ferric perchlorate (0.002*M*), sulpholsalicylic acid (0.002*M*) and aluminium perchlorate were mixed. The required amounts of sodium perchlorate to adjust the ionic strength and perchloric acid or NaOH to adjust the p_H to 2.4, when diluted, were added and the mixture diluted to 50 c.c. in each case with distilled water. Simultaneously a 'blank' solution was prepared by mixing the same amounts of ferric perchlorate and sulphosalicylic acid as in the previous ones, but without aluminium perchlorate. The p_H and ionic strength of this mixture were also adjusted to the same values as in the previous ones. From the optical densities of these mixtures, the dissociation constants of the ferric and aluminium complexes were calculated.

The extinction coefficient of the ferric complex was also determined at different ionic strengths by measuring the optical densities of the solutions in which the ratio of $[Fe^{3+}]$ to [sulphosalicylate] was 1 : 8 or 1 : 9 and *vice versa*. As expected, the ionic strength was found to have no effect upon the extinction coefficient, the average value of which came out to be 2035. It may be noted that the value reported by Foley and Anderson (*loc. cit.*) for the extinction coefficient of the complex at p_H 2.38 was 753, but from their curves the value of extinction coefficient on calculation came to ~ 2000.

Discussion

Taking the extinction coefficient of ferric sulphosalicylate to be equal to 2036, the dissociation constant of the ferric complex has been calculated at various ionic strengths. These are recorded in column 6 of the table and the average values in column 7. It may be interesting to compare our values with those of Foley and Anderson (*loc. cit.*). They obtained a value of $1.3 \pm 0.2 \times 10^{-5}$ for the dissociation constant of the complex at p_H 2.38 and ionic strength of about 0.06, whereas in the present investigation at $\mu = 0.05$ and $p_H = 2.4$, the average value obtained was 1.39×10^{-5}. In view of the experimental limitations the agreement is good. The values of dissociation constant show a trend to increase with ionic strength.

We have assumed the aluminium sulphosalicylate complex to be of the 1 : 1 type, as Job's method cannot be applied under the present experimental conditions. Such an assumption seems to be justified in view of the identical ferric complex formed under similar conditions. Also Lasater and Anderson (*loc. cit.*) have found the aluminium complex to be of the 1 : 1 type at p_H 4.0, and at p_H 2.4 the formation of higher complex, *i. e.* (1 : 2), is least probable. So the dissociation constant of the aluminium sulphosalicylate complex has been calculated, taking it to be of the 1 : 1 type. The dissociation constants at different ionic strengths are shown in column 8 and the average values at each ionic strength, in column 9 of the table. Here also it is found that the dissociation constants increase with ionic strength. The value of the dissociation constant of the same complex, reported by the previous workers, is about 5×10^{-4}. The comparison of this value with ours became difficult as these workers did not record the ionic strength. But on the average, our values are about four times higher. This difference may be ascribed to the following factors. Firstly, Anderson *et al.* (*loc. cit.*) have worked with

copper sulphate solution. In a recent communication Monk *et al.* (*Trans. Faraday Soc.*, 1956, **52**, 816) have reported the dissociation constant of $CuSO_4$ to be 4.5×10^{-3} (5×10^{-3}), which is almost of the same order as that reported for the aluminium sulphosalicylate complex. The presence of sulphate ions might have vitiated their results.

Anderson *et al.* (*loc. cit.*) worked at p_H 4, whereas the present work was carried out at p_H 2.4. This difference in p_H might also be the cause of the difference noted. It may be pointed out at this stage that due to the hydrolysis of ferric perchlorate, ferric sulphosalicylate could not be used as indicator for the displacement measurements at p_H 4.

Further, as mentioned earlier, they have not recorded the ionic strength of the solution. It is probable that a large difference in the ionic strength might bring about the difference observed. Apparently the best check would be to determine the nature as also the dissociation constant of the complex from measurements in the ultraviolet at the desired p_H and ionic strength. Work along this line is already in progress for the aluminium sulphosalicylate and such other complexes.

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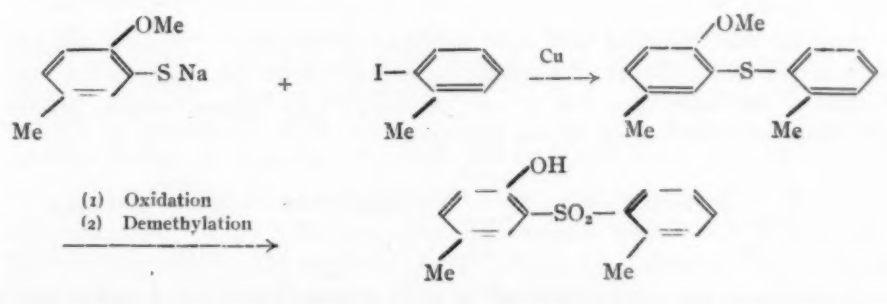
FRIES REACTION WITH ARYL *o*-TOLUENESULPHONATES AND ARYL ALKANESULPHONATE

By V. Baliah and Mrs. Aleykutty Mathew

Phenyl *o*-toluenesulphonate undergoes the Fries reaction when heated with anhydrous aluminium chloride to afford a mixture of *o*- and *p*-hydroxysulphones. *p*-Tolyl and *p*-chlorophenyl *o*-toluenesulphonates isomerise to 2-hydroxy-5:2′-dimethyldiphenylsulphone and 5-chloro-2-hydroxy-2′-methyldiphenylsulphone respectively. Aryl alkanesulphonates do not undergo the reaction.

The work reported in this communication is a continuation of what has been reported earlier (Aleykutty and Baliah, *Curr. Sci.*, 1953, **22**, 307; this *Journal*, 1954, **31**, 513; 1955, **32**, 773; 1956, **33**, 189). The Fries rearrangement of phenyl, *p*-tolyl and *p*-chlorophenyl *o*-toluenesulphonates has been studied in the present investigation. When phenyl *o*-toluenesulphonate was heated with anhydrous aluminium chloride at 130-40° for 45 minutes, it isomerised to the extent of 47%. At a lower temperature (120-25°) the isomerised product was only 31%. Both the *o*- and *p*-hydroxysulphones were present in the product. The difference in their solubilities in non-polar solvents like benzene and ligroin was not much and, hence, easy separation could not be effected. Repeated fractional crystallisation from ligroin gave 2-hydroxy-2′-methyldiphenylsulphone alone in a pure condition. The *p*-isomer could not be purified. The two isomers were synthesised unequivocally and the identity of the Fries product, which was obtained pure, was established by comparison with the synthetic sample.

The Fries reaction of *p*-tolyl *o*-toluenesulphonate furnished a hydroxysulphone which was identical with 2-hydroxy-5:2′-dimethyldiphenylsulphone, synthesised as follows:



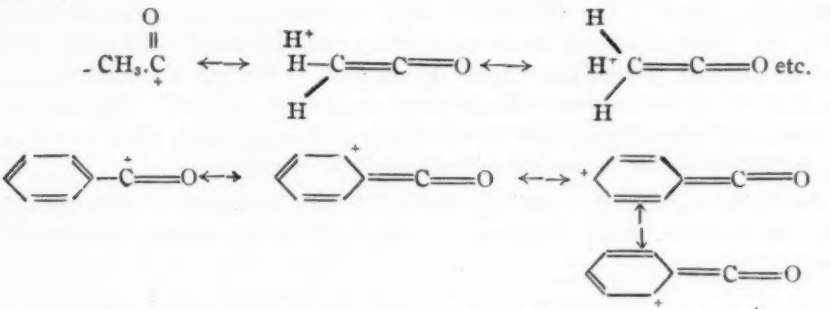
p-Chlorophenyl *o*-toluenesulphonate isomerised analogously, yielding 5-chloro-2-hydroxy-2′-methyldiphenylsulphone. The identity of this sulphone also has been established by a similar unambiguous synthesis.

A striking observation made in the present investigation is the failure of aryl alkanesulphonates to undergo the isomerisation. This difference in the behaviour of

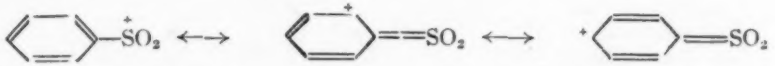
aryl arenesulphonates and aryl alkanesulphonates becomes significant when we bear in mind that no such difference exists in the case of aryl esters derived from aromatic and aliphatic carboxylic acids.

Attempts were made to isomerise *p*-tolyl methanesulphonate, *p*-tolyl ethanesulphonate and *p*-tolyl phenylmethanesulphonate. In no case the reaction occurred. For example, *p*-tolyl ethanesulphonate, when heated with aluminium chloride in nitrobenzene at 140-50° for 3 hours, gave only an intractable tar. Lowering of the temperature and reducing the time of heating did not prove helpful. It appeared worthwhile to try a milder catalyst. With zinc chloride, even at 160°, the sulphonate remained unchanged.

Generally, the esters of sulphonic acids isomerise less readily than the esters of carboxylic acids. Further, we find that the esters of aliphatic sulphonic acids undergo no isomerisation at all. This difference in the behaviour of sulphonates and carboxylic esters seems to arise from the difference in the stabilities of the cation intermediates in the reaction. The generally accepted mechanism of the Fries reaction postulates the formation of an acyl carbonium ion as an intermediate, and this ion makes an electrophilic attack on the aromatic nucleus. The acyl carbonium ions derived from aliphatic and aromatic carboxylic acids can have the following hyperconjugated or resonance structures:



They are thus stabilised and their formation is facilitated. Though resonance structures such as (II), (III) etc. are possible for the ions derived from sulphonates, their formation is less facile than that of acyl carbonium ions because resonance involves double bond formation between sulphur and carbon.



(I) (II) (III)

According to the overlap principle a $2p$-$2p$ π-bond is more easily formed than a $3p$-$2p$ π-bond. Hence, the acyl ions result more easily than the arene- or alkane-sulphonyl ions.

EXPERIMENTAL

The Fries Rearrangement of Phenyl o-Toluenesulphonate.—An intimate mixture of phenyl *o*-toluenesulphonate (37.2 g.) and finely powdered anhydrous aluminium

chloride (30 g.) was heated at 130-40° for 45 minutes. After cooling, the product was treated with HCl in crushed ice and extracted with ether. The ether solution was then extracted with a 10% solution of NaOH until most of the alkali-soluble product was removed from it. The combined alkali extract was acidified. The precipitated hydroxysulphone, which was in a semi-solid condition, hardened after drying in a vacuum desiccator. It weighed 17 3 g. (47%). The product, on extraction with hot ligroin and evaporation of the solvent, gave 6.7 g. of a colorless product which on repeated crystallisation from ligroin melted at 125-26°. There was no depression in melting point on admixture with a synthetic sample of 2-hydroxy-2′-methyldiphenylsulphone (*vide infra*). (Found : C, 62.4 ; H, 4.9. Calc. for $C_{13}H_{12}O_3S$: C, 62.9 ; H, 4.8%). The ligroin-insoluble portion was chiefly the isomeric *p*-hydroxysulphone. It remained as a semi-solid and could not be crystallised from any of the common solvents.

2-Methoxy-2′-methyldiphenyl Sulphide.—To a solution of sodium ethoxide (1.9 g. of sodium in 25 c.c. of absolute ethanol) *o*-thiocresol (10 g.) was added and evaporated to dryness. This was treated with *o*-iodoanisole (20.8 g.) and copper powder (1 g.) and heated at 230-40° for 3 hours. The product, after cooling, was mixed with zinc dust (10 g.) and sulphuric acid (1 : 1 ; 50 c.c.) and steam-distilled. The residue was extracted with ether, evaporation of which gave 17.4 g. (87%) of the sulphide. It boiled at 174°/12.5 mm and melted at 55-56°. (Found : C, 72.8 ; H, 6.3. $C_{14}H_{14}OS$ requires C, 73.1 ; H, 6.1%).

2-Methoxy-2′-methyldiphenylsulphone.—A solution of the foregoing sulphide (4.6 g.) in glacial acetic acid was treated with excess of a 5% $KMnO_4$ solution and kept aside for 30 minutes. It was decolorised with SO_2, diluted with water and cooled. The sulphone separating was filtered off and washed with water, yield 4.8 g. (92%). On crystallising from ethanol it melted at 140-42°. (Found : C, 64.3 ; H, 5.3. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3%).

2-Hydroxy-2′-methyldiphenylsulphone.—A mixture of the above sulphone (2.62 g.) and HI (*d* 1.7, 8 c.c.) was heated at 190-200° for 4 hours. On cooling, a reddish brown viscous mass, which solidified gradually, was obtained. It was dissolved in a 10% solution of NaOH, filtered and the filtrate acidified. The hydroxysulphone was obtained in quantitative yield (2.4 g.). After crystallising from ethanol it melted at 125-26°. (Found : C, 62.9 ; H, 5.1. $C_{13}H_{12}O_3S$ requires C, 62.9 ; H, 4.8%).

4-Methoxy-2′-methyldiphenyl sulphide was prepared from 4-iodoanisole (23.8 g.) and *o*-thiocresol (10 g.). The experimental procedure was the same as that used for the 2-methoxy isomer. The yield was 17 g. (92%), b.p. 150-52°/12 mm. (Found : C, 72.9 ; H, 5.9. $C_{14}H_{14}OS$ requires C, 73.1 ; H, 6.1%).

4-Methoxy-2′-methyldiphenylsulphone.—Oxidation of the foregoing sulphide with $KMnO_4$ solution afforded the sulphone in almost quantitative yield. It was necessary to warm the solution with $KMnO_4$ for a few minutes. The sulphone separated as an oil which solidified very slowly. After crystallising from ethanol it melted at 83-84°. (Found : C, 63.9 ; H, 5.6. $C_{14}H_{14}O_3S$ requires C, 64.1 H, 5.3%).

The above sulphone was heated with hydriodic acid at 180° for 3 hours. The product so obtained was completely soluble in alkali. It remained as a semi-solid for more than a month. It could not be crystallised.

p-*Chlorophenyl* o-*toluenesulphonate* was prepared from *p*-chlorophenol and *o*-toluenesulphonyl chloride in the usual way. Crystallisation from ethanol gave needles, m.p. 63-65°. (Found : C, 55.2 ; H, 3.7. $C_{13}H_{11}O_3ClS$ requires C, 55.2 ; H, 3.9%).

The Fries Rearrangement of p-*Chlorophenyl* o-*Toluenesulphonate.*—The sulphonate (5.6 g.) was heated with anhydrous aluminium chloride (8 g.) at 110-20° for 45 minutes. The product, when worked up as usual, gave the hydroxysulphone (0.8 g., 14%). On crystallisation from ethanol it melted at 111-12° with or without a synthetic sample of 5-chloro-2-hydroxy-2′-methyldiphenylsulphone. (Found : C, 51.7 ; H, 4.3. Calc. for $C_{13}H_{11}O_3ClS,H_2O$: C, 51.9 ; H, 4.3%).

5-*Chloro-2-methoxy-2′-methyldiphenyl sulphide* was prepared from *o*-iodotoluene (21.8 g.) and 5-chloro-2-methoxythiophenol (Gauntlette and Smiles, *J. Chem. Soc.*, 1925, **127**, 2745) (17.4 g.) by heating in the presence of copper ; yield 21.3 g. (81%), b.p. 178-80°/8 mm. (Found : C, 63.1 ; H, 5.0. $C_{14}H_{13}OClS$ requires C, 63.5 ; H, 4.9%).

5-*Chloro-2-methoxy-2′-methyldiphenylsulphone.*—Oxidation of the foregoing sulphide in acetic acid with $KMnO_4$ solution gave this compound (85%). After crystallising from ethanol it melted at 139-40°. (Found : C, 56.9 ; H, 4.7. $C_{14}H_{13}O_3ClS$ requires C, 56.7 ; H, 4.4%).

5-*Chloro-2-hydroxy-2′-methyldiphenylsulphone* was obtained by demethylating the above sulphone with HI in 92% yield. On crystallisation from ethanol it melted at 111-12°. (Found : C, 51.7 ; H, 4.0. $C_{13}H_{11}O_3ClS,H_2O$ requires C, 51.9 ; H, 4.3%).

The Fries Rearrangement of p-*Tolyl* o-*Toluenesulphonate.*—By heating the sulphonate (5.24 g.) with aluminium chloride (4 g.) at 130-40° for 45 minutes and working up the product as usual, 1.94 g. (37%) of the *hydroxysulphone* was obtained. After crystallising from ethanol it melted at 153-54° with or without a synthetic sample of 2-hydroxy-5 : 2′-dimethyldiphenylsulphone. (Found : C, 63.7 ; H, 5.2. Calc. for $C_{14}H_{14}O_3S$: C, 64.1 ; H, 5.3%).

2-*Methoxy*-5 : 2′-*dimethyldiphenyl sulphide* was obtained from 2-methoxy-5-methylthiophenol (15.4 g.) and *o*-iodotoluene (21.8 g.) in 86% yield. It melted at 64-65° after crystallising from acetic acid. (Found : C, 73.8 ; H, 6.4. $C_{15}H_{16}OS$ requires C, 73.8 ; H, 6.6%).

2-*Methoxy*-5 : 2′-*dimethyldiphenylsulphone.*—Oxidation of the foregoing sulphide afforded this compound in 85% yield. On crystallisation from acetic acid it melted at 133-35°. (Found : C, 65.6 ; H, 6.2. $C_{15}H_{16}O_3S$ requires C, 65.2 ; H, 5.8%).

2-*Hydroxy*-5 : 2′-*dimethyldiphenylsulphone.*—Demethylation of the foregoing sulphone yielded this compound in almost quantitative yield. On crystallising from ethanol it melted at 153-54°. (Found : C, 63.8 ; H, 5.0. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3%).

p-*Tolyl Ethanesulphonate.*—Ethanesulphonyl chloride was added slowly to *p*-cresol in a 5% solution of NaOH and shaken well for a few minutes. The sulphonate was obtained in 86% yield ; b.p. 153-54°/13·5 mm. (Found : C, 54.4 ; H, 5.9. $C_9H_{12}O_3S$ requires C, 54.0 ; H, 6.0%).

p-*Tolyl Phenylmethanesulphonate.*—Esterification of *p*-cresol with phenylmethanesulphonyl chloride (Johnson and Sprague, *J. Amer. Chem. Soc.*, 1936, **58**, 1348) furnished this compound. After recrystallising from ethanol it melted at 76-78°. (Found : C, 63.9 ; H, 5.5. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3%).

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CELLULOSE-ION EXCHANGE RESINS FOR PURIFICATION AND FRACTIONATION OF PROTEINS. PART I. COBALAMIN PROTEIN FROM HOG GASTRIC MUCOSA*

By Pijush Kanti Choudhury**

Cobalamin protein from hog gastric mucosa has been purified by adopting cellulose-ion exchange chromatography with gradient elution technique. The protein appears to consist of at least two protein components.

The preparation and properties of a cobalamin protein (complex of a protein component plus vitamin B_{12}) from hog gastric mucosa have been reported by Stern *et al.* (*Biochim. Biophys. Acta*, 1954, **13**, 144). A similar cyano-protein complex (Gregory and Holdsworth, *Nature*, 1954, **173**, 830) from sow's milk and desiccated pig stomach has also been reported. By employing cellulose-ion exchange chromatography with gradient elution technique, we have recently observed that the cobalamin protein or the red protein appears to consist of at least two protein components, and it has been considerably purified by the action of cellulose-ion exchangers.

Experimental

The cellulose-ion exchange adsorbents were prepared according to the method of Peterson and Sober (*J. Amer. Chem. Soc.*, 1956, **78**, 751). The anion exchanger, diethylaminoeth lcellulose (DEAE-), was specially suited for our work. The efficiency of this anion exchanger was tested by an actual separation of artificial mixtures of albumin with bromophenol blue and hemoglobin, and hemoglobin with cytochrome c, before it was used for the purification and fractionation of cobalamin protein. The preliminary separation, as tested by spectrophotometry, was found to be highly satisfactory. The elution technique employed was similar to that of Sober and Peterson (*ibid.*, 1956, **78**, 756) for the fractionation of their serum protein by cellulose-anion exchanger.

Two cobalamin protein preparations, having different concentrations of vitamin B_{12}, were used. The following fractions were prepared by adding crystalline cyano-cobalamin to hog gastric mucosa :

1. Sample A : I.F. 762, partially purified fraction (B_{12} content 3.7μ g. per mg.),
2. Sample C : I.F. 1732, very impure fraction (B_{12} content 1.8μ g. per mg.).

Method.—The chromatographic column was prepared in the following way. Alcohol-wet DEAE- cellulose (5 g.) was made a slurry with 40 c.c. of sodium phosphate buffer solution at p_H 7.7 and ionic strength 0.02 and poured into a column (13 × 1cm) to maintain a height of 10 cm. The initial packing was done under gravity, but towards the end a nitrogen pressure of 10 lbs./sq. in. was applied to make the column more compact. About 1.70% solution (5 c.c. each) of samples A and C in sodium phosphate

* This work was carried out in the laboratory of Prof. Kurt G. Srern, who died suddenly in Landon in Feb. 3, 1956, before it was completed.

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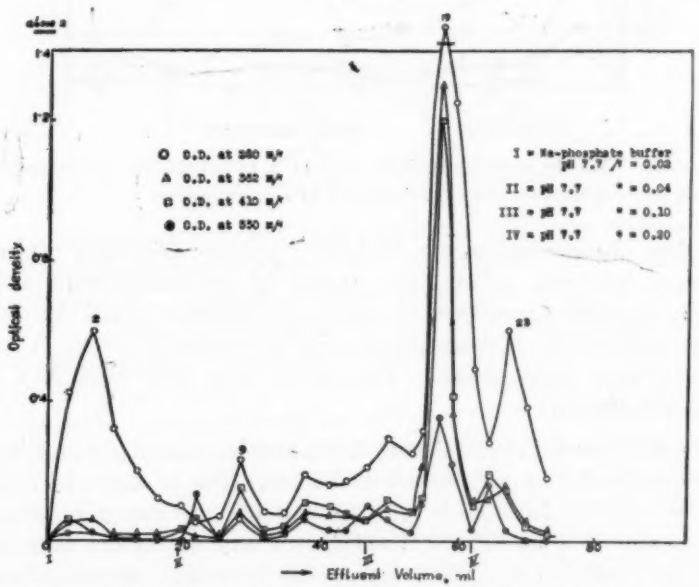
buffer solution of the same p_H and ionic strength was added dropwise to the column (10 × 1 cm) of DEAE- cellulose. A deep red zone of about 1 cm in height was formed when the addition of the solution was complete. This was then eluted with sodium phosphate buffers of increasing ionic strengths (0.02, 0.04, 0.1 and 0.2). To obtain a convenient efflux rate of at least 10 to 12 c.c./hr., the hydrostatic head was adjusted to 60 cm with an additional long thin column. Successive fractions of 3 c.c. were then collected in a fraction collector at a flow rate of 3 c.c./15 mins. (viz., 12 c.c/1 hr.). Buffer changes were effected by completely drawing off the solutions by a syringe with a long needle and replacing it by the buffer of next higher ionic strength. Strictly speaking, this was not a gradient elution but a stepwise change. In the case of sample C, which was extremely viscous, the effluents were collected under gentle suction as the flow rate under the hydrostatic pressure was too low.

DISCUSSION

In Figs. 1 and 2, we have plotted effluent volumes of samples A and C against their optical densities at 280, 362, 410 and 550 mμ respectively. The optical density at 280 mμ is largely due to protein, at 362 and 550 mμ to cyano-cobalamin (Gregory and Holdsworth, *loc. cit.*) and at 410 mμ to hemochromogen, an impurity. It will be seen from Fig. 1 that the maximum concentration of red protein is in fraction 19. Two

FIG. 1

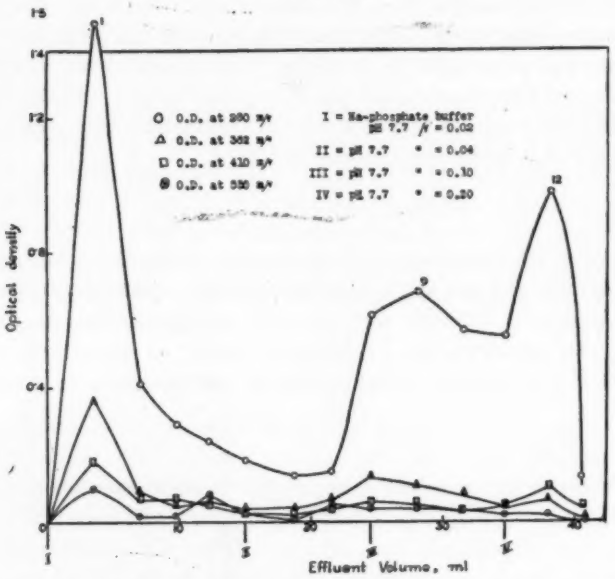

O O.D. at 280 mμ
Δ O.D. at 362 mμ
□ O.D. at 410 mμ
● O.D. at 550 mμ
I = Na-phosphate buffer pH 7.7 μ = 0.02
II = pH 7.7 μ = 0.04
III = pH 7.7 μ = 0.10
IV = pH 7.7 μ = 0.20
Optical density
Effluent Volume, ml

Sample A : Conc. 1.72% in sodium phosphate buffer; 2, 19, 23 indicate No. of tubes collected in the fraction collector showing the maximum conc. of protein and cobalamin protein.

other protein maxima occur in fractions 2 and 23. In fraction 2, however, the concentration of cyano-cobalamin is very low. This may be the reason why this

solution is practically colorless. The solution of fraction 23 is pink due to a somewhat greater concentration of cyano-cobalamin while the protein concentrations of the two fractions are practically the same in both the cases. Similarly in Fig. 2 there are three peaks at 280 mμ, indicating three protein components.

FIG. 2


O O.D. at 280 mμ
Δ O.D. at 362 mμ
□ O.D. at 410 mμ
● O.D. at 550 mμ
I = Na-phosphate buffer pH 7.7 μ = 0.02
II = pH 7.7 " = 0.04
III = pH 7.7 " = 0.10
IV = pH 7.7 " = 0.20
Optical density
Effluent Volume, ml

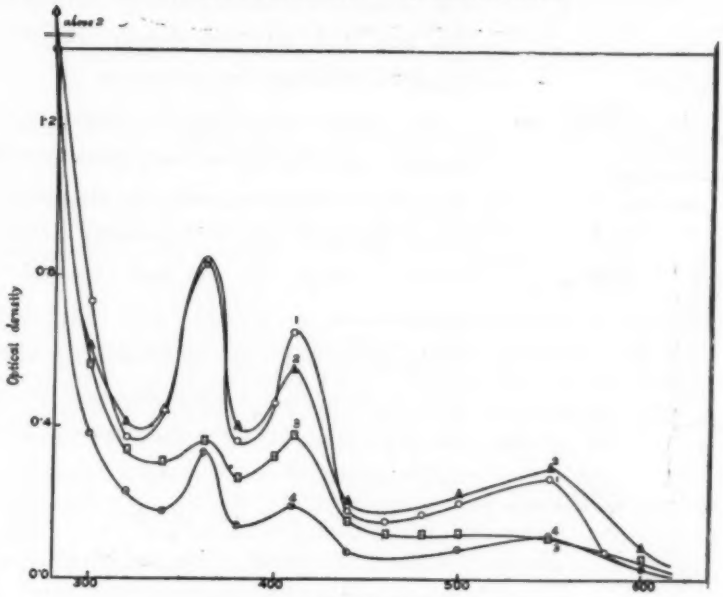
Sample C: Conc. 1.80% in sodium phosphate buffer; 1, 9, 12 indicate No. of tubes collected in the fraction collector showing the max. conc. of protein and cobalamin protein.

For further characterisation, the isolated fractions containing the maximum concentrations of cobalamin protein were studied by spectrophotometry and electrophoresis. The complete spectrum of fraction 19 (from sample A) and fraction 1 (from sample C) are shown in Fig. 3, along with the original solutions of samples A and C from which these fractions were obtained. The spectra were determined in a Beckman quartz spectrophotometer.

It will be seen from Fig. 3 that the cobalamin protein, particularly in sample C, has been considerably purified by cellulose-ion exchanger. This is shown by their substantially reduced optical densities at 410 mμ and by the clarity of the solutions. The original solutions from samples A and C were very turbid and they had to be clarified for spectrophotometric measurements by prolonged centrifugation at high speed. In contrast to the original solutions, DEAE-cellulose fractions were obtained optically clear. The considerably reduced peak at 410 mμ in curve No. 4 retaining the same peaks at 362 and 550 mμ with that of the original curve (No. 3) shows that substantial purification has been effected.

FIG. 3

Absorption spectra of purified fractions of cobalamin protein as compared with their original solutions.

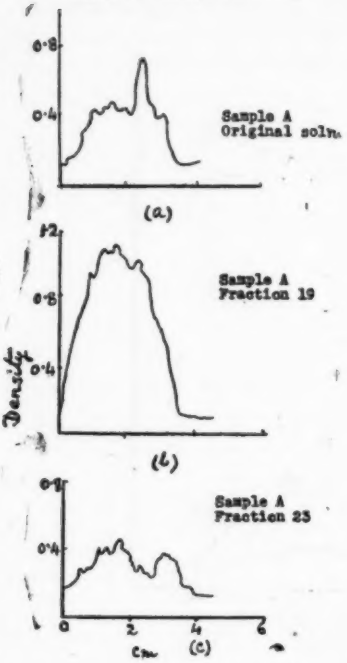


Spectrum No. 1 : Sample A.
Spectrum No. 2 : „ fraction 19.
Spectrum No. 3 : Sample C.
Spectrum No. 4 : „ fraction 1.

The electrophoretic mobility and separation of the cobalamin proteins was studied by Spinco Paper Electrophoresis (Block *et al.*, "A Manual of Paper Chromatography and Paper Electrophoresis", Academic Press Inc., New York, 1955). A model R type cell was used for this purpose. The coloured fractions (1 c.c.) were freeze-dried and the dry residue dissolved in 1 drop of sodium phosphate buffer at p_H 7.7 and ionic strength 0.02. Barbiturate buffer at p_H 8.6 with ionic strength 0.075, a constant current of 0.75 ma for 8 paper strips and a run of 16 hours per cell were used throughout. The original solution (1 c.c. each) from samples A and C after freeze-drying was simultaneously run for comparison. In each case duplicate strips were run. After the strips had been thoroughly dried at 100° for 1 hour, these were stained with Amido black (300 mg. Amido schwarz 10B dissolved in 45 c.c. of glacial acetic acid and 405 c.c. of absolute methanol) and destained with a mixture of 10% glacial acetic acid and 90% absolute methanol till no more dye could be washed out. The strips were then dried at room temperature. The paper strip patterns were then evaluated by an Electronic Densitometer, model 525 (Photo Volt Corporation), fitted with a graphic recorder "Servo" model 100. The patterns are shown in Fig. 4. The same patterns were obtained on repetition.

FIG. 4

Electrophoretic pattrern of sample A and fracitions.



A comparison of the electrophoretic patterns from the fractions with their original solution will show that at least two cobalamin protein components exist, and they have been successfully isolated by the action of cellulose-anion exchanger.

The sample C being highly impure, the electrophoretic patterns were not very distinct. However, a colorless protein omponent has also been isolated cfrom sample C. This is probably a mucoprotein which accounts for the high viscosity of this solution.

Microbiological assay of vitamin B_{12} and clinical tests on the purified fractions could not be completed at this time but are in progress and will be reported in due course.

The author is deeply indebted to Prof. Herman Mark, Prof. Gerald Oster and Dr. H. P. Frank of Polymer Research Institute, New York for their encouragement and invaluable assistance in completing the work after the sudden and unexpected death of Professor Kurt G. Stern in London.

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MEASUREMENT OF EXCHANGEABLE IONS IN DIFFERENT AFFINITY LEVELS

By A. Chatterjee

The difference in the exchangeability of a particular cation at different degrees of saturation has been demonstrated by allowing the heteroionic systems, NH_4 (Ba) -clay and NH_4 (Na) -clay to equilibriate with H-resin in cellophane bags. The existence of 'loosely' and 'firmly' bound conditions of the same cation is clearly noticeable from the experimental data. This confirms the earlier observations of Mukherjee and co-workers using electrolytes for the purpose of exchange.

The same cation is adsorbed by different clay minerals with different bonding energies because of the difference in the lattice forces, but with regard to the same clay mineral also, a particular cation may be adsorbed with different bonding energies. This was suggested by Wiegner and Mitchell (*J. Land.*, 1912, **60**, 111, 197) in the case of permutites and extended by Wiegner (Trans. Int. Cong. Soil Sci., 3rd Congr., Oxford, 1935, p. 111), Ganguly and Mukherjee (*J. Phys. Coll. Chem.*, 1951, **55**, 1429) and Marshall (*Soil Sci.*, 1948, **65**, 57) in the case of clay minerals. Bottini (*Kolloid Z.* 1937, **78**, 68) measured the amount of ammonia evolved from $Ca-NH_4$-clay and NH_4-Ca-clay by thermal treatment and found in agreement with the earlier observation that the NH_4^+ ion was held differently in these two clays. Vanselow (*Soil Sci.*, 1932, **33**, 95) with the same mixed clay determined the equilibrium constants and found them to differ, proving that the release of ions depends on the priority of adsorption on the clay surface. The existence of H^+ ions in definite affinity levels on the surface of clay minerals has been established by the researches of Mukherjee and co-workers (Special publication, I.A.-C.S. Calcutta, No. XIII, 1947), who used electrolytes for purposes of exchange. In the present paper, as noted below, an acid exchanger, separated by a cellophane bag, has been used for the same purpose.

From a close study of the neutralisation curves and salt titrations or exchangeable isotherms of clay acids and salts, it is now well established that the exchangeable ions are not of equal bonding energies (Marshall, "The Colloid Chemistry of Silicate Minerals"; Mitra, *Indian Soc. Soil Sci. Bull.*, 1941-42, **4**, 21). Several categories of the same cation, saturating the clay, have been recognised. This also finds support from the crystalline structure of the clay minerals. The nutrient ions present in the soil are supposed to be made available to the plant by means of an exchange process. In that case the availability will be influenced by the exchangeability of the different category of ions of the clays. The exchangeability of the ions is determined by their bonding energy to the clays. Consequently, the cations of the clays with higher bonding energies will exchange for a particular exchanging cation, if the concentration of the latter is gradually increased. In the plant-soil relationship it is assumed that the exchanging cation is hydrogen, which is liberated by the plant roots.

The experimental arrangement that is likely to simulate plant-root fairly closely is to have a more or less solid acid exchanger which may be allowed to equilibriate under proper conditions with the soil or the exchange material present in it, *i.e.*, the colloidal clays. Such an arrangement has been worked out by Brown and Albrecht (Res. Buil. No. 477, College of Agric. Univ. of Mo., 1950). They used a collodion membrane to separate a soil or the clay, saturated with one or more cations, from a desaturated clay of the montmorillonite type having high b.e.c. The amount of the cations extracted by the desaturated clay, which simulated the acidic environment of the plant-roots, was then determined. Brown *et al.* (*loc. cit.*) have established that the different cations in a soil or clay exist in "suites", depending obviously on their respective bonding energies. Working with a homoionic soil or clay, *i.e.*, saturated with one kind of cation, they observed different rates of extraction over, more or less, definite range of saturation.

In this paper, the technique of Brown and Albrecht (*loc. cit.*) was used to observe the difference in exchangeability of some binary clays, which were saturated with different proportions of a pair of cations but having somewhat known exchange characteristics. According to the earlier observations of Renold (*Koll. - Chem. Beih.*, 1936, **43**, 1), Wiegner (*loc. cit.*) and Ganguly and Mukherjee (*loc. cit.*), the exchangeability of a cation in presence of another is determined by the manner of its addition. Thus, the cation that is added first is more difficult to exchange than the one added next ; so that a binary clay, NH_4—Ba clay, is different from a Ba—NH_4 clay, having the same proportion of the cations. The difference is more prominent with regard to exchangeability or properties closely related to it. Ganguly and Mukherjee (*loc. cit.*) have further shown that the difference in exchangeability becomes evident only after a "critical ratio" of the two ions concerned is exceeded. The binary clays containing varying proportions of Ba^{2+} and NH_4^+ and Na^+ and NH_4^+ ions have been prepared in the following manner.

Experimental

To a known amount of H-clay, the calculated amount of one of the bases required to attain a definite extent of saturation was added first in the form of hydroxide and the mixture was allowed to equilibriate. After about a week or more, the other base was similarly added to complete the saturation and allowed to come to equilibrium. In this way, a pair of clays, e.g., Ba—NH_4-clay and NH_4—Ba-clay was obtained. Three different ratios, viz., 70 : 30, 50 : 50 and 30 : 70, were used for the same pair of cations. Usually the cation written next to 'clay', e.g. NH_4^+ in Ba—NH_4-clay, is purported to be more difficult to exchange than the NH_4^+ written away from 'clay', viz., NH_4—Ba-clay. The same is true of Ba^{2+} ions and other pairs of ions.

The clays were then allowed to exchange for H^+ ions of H-resin taken in cellophane bags by immersing them into the clay suspensions. The bottles containing the clays were thoroughly paraffined so as to prevent evaporation of water from the contents of the bottles. The amount of H-resin was so adjusted that it corresponded to the

total amount of bases present in the clay, *i.e.*, in the symmetry concentration. Sufficient time was allowed to attain equilibrium, tested by the constancy of p_H value of the clay suspension. The total amount of H^+ ions, exchanged for the cations, was determined by the KCl-KOH method using the clay system. In addition, the total amount of exchangeable ammonia, still present in the clay after exchange, was leached out and determined by nesslerisation and comparison of the colour produced by a standard solution of NH_4Cl. The amount of the other cation, viz., Ba^{2+} and Na^+, was then obtained by the difference (total m.e. originally present) - (M.e.H^+ + m.e.NH_4^+). The amounts of the two cations present in the binary systems and expressed as percentage of the total as well as of the respective cation of the mixed clay are shown in Tables I and II against the proportion of the two cations.

TABLE I

Types of clay.	Ratio NH_4:Ba.	% Ammonia released of the total		% Barium released of the total	
		exchangeable ions.	exchangeable ammonia.	exchangeable ions.	exchangeable Ba.
NH_4—Ba-clay	30:70	16.7	55.6	9.1	13.0
Ba—NH_4-clay		5.2	17.3	16.0	22.9
NH_4—Ba-clay	50:50	20.0	40.0	4.5	9.0
Ba—NH_4-clay		19.0	38.0	5.4	10.8
NH_4—Ba-clay	70:30	27.6	39.4	0.4	1.3
Ba—NH_4-clay		23.4	33.4	0.4	1.3

TABLE II

Types of clay.	Ratio NH_4:Na.	% Ammonia released of the total		% Sodium released of the total.	
		exchangeable ions.	exchangeable NH_4.	exchangeable ions.	exchangeable Na.
NH_4—Na-clay	50:50	16.3	32.6	16.6	33.2
Na—NH_4-clay		2.9	5.8	24.5	49.0
NH_4—Na-clay	70:30	11.5	16.4	15.9	53.0
Na—NH_4-clay		9.9	14.1	23.4	78.0

DISCUSSION

On comparing the NH_4—Ba-clay and the Ba—NH_4-clay having the same proportion of NH_4^+ and Ba^{2+}, it is found that NH_4^+ in the former is exchanged in a larger amount than in the latter. On the other hand, Ba^{2+} in the latter is more readily replaced by H^+ ions of H-resin than in the former. This general observation fails in the case of the mixed clays in which Ba^{2+} constitutes only 30% ; this means that at or below 30%, Ba^{2+} is adsorbed in the same state of bonding in both the mixed clays. This is somewhat similar to the "critical ratio" observed earlier by Ganguly and Mukherjee

(*loc. cit.*), but the value of the ratio is less than that found for bivalent cations. In the case of Na—NH_4- and NH_4—Na-clays, the differentiation between the exchangeability of either Na^+ or NH_4^+ at the same porportion is similarly evident. It is also evident from the data that the same cation is not exchangeable to equal extents although present in the same porportion, showing that it is not adsorbed by the clay in identical manner ; perhaps the bonding energy is different.

Sincere thanks of the author are due to Dr. S. K. Mukherjee, Applied Chemistry, Department, Calcutta University, for his helpful suggestions and continued interest in the problem and for providing laboratory facilities.

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EXCHANGE OF PHOSPHATES ADSORBED BY CLAYS FOR OTHER ANIONS

By A. Chatterjee

Anion-exchange measurements have been carried out with particular reference to phosphate ions, partly because it is important as a plant nutrient and partly because it has the peculiar property of becoming unavailable or fixed under certain conditions by clays and clay minerals. Anion-exchange resins saturated with hydroxyl, oxalate, citrate and fluoride ions have been used for the exchange measurements. Hydroxyl, citrate and oxalate ions of the anionic resin exchange themselves for phosphate in varying extents, but fluoride is almost incapable of releasing phosphate under the conditions of the experiment.

It has been reported (Midgley, *Soil Sci. Soc. Amer. Proc.*, 1940, **5**, 24; Sinha, this *Journal*, 1956, **33**, 415) that kaolinites and kaolinitic clays adsorb larger amounts of phosphates than montmorillonitic or other types of clays. The phosphate adsorption capacity (p.a.c.) of kaolinite can appreciably be increased by grinding the mineral alone or in presence of phosphates (Sieling, *Soil Sci. Soc. Amer. Proc.*, 1946, **11**, 161). The reaction between phosphates and the kaolinitic clays may, under certain conditions, be so drastic that decomposition of kaolinite occurs in varying degrees. The major portion of phosphate adsorbed by kaolinite remains unavailable towards plants or extracting solutions. It is 'fixed', so to say. About the mechanism of "fixation", no definite conclusions have yet been arrived at. It is, however, reported that added phosphates can be exchanged almost entirely for anions such as fluoride, citrate, oxalate and hydroxyl ions (Marshall, "The Colloid Chemistry of the Silicate Minerals"). Phosphate adsorption by clay minerals was earlier reported by Chatterjee and Dutta (*Indian J. Soil Sci.*, 1951, **2**, 224).

In the present investigation an attempt has been made to measure the available phosphates by setting up an equilibrium exchange reaction between the adsorbed phosphates on the kaolinitic clays and the anion-exchange resins, saturated with anions like F^-, OH^-, citrate^{3-} and $C_2O_4^{2-}$, according to the technique of Brown and Albrecht (Res. Bull. No. 477, College of Agric., Univ. of Mo., 1950).

The advantage of using the exchanging anionic resin lies in the fact that exchange will take place against a known anion, quite unlike the soil, which is likely to contain more than one kind of anions. Since dissolution and complex formation (Haseman *et al.*, *Soil Sci.*, 1950, **70**, 257) are eliminated in this way, the exchange behaviour of the process may otherwise be regarded as simulating plant-root-soil system and, hence, will measure strictly that part alone which is available by exchange.

Experimental

The electrodialysed clay fraction ($<0.5\mu$) of a sample of kaolinite from Rajmahal, Bihar State, was phosphatised by adding 0.1*N*-H_3PO_4, adjusting the p_H to 4.0 with NaOH solution and allowing several days for the reaction to proceed. The phospha-

tised clay was then washed free of the excess of phosphate with double-distilled water, care being taken to prevent hydrolysis of the clay-phosphate complex by excessive washing. The p_H value of about 4% suspension, thus obtained in double-distilled water, varied between 5.5 and 6.0.

The total amount of phosphate adsorbed by the kaolinite clay (or p.a.c.) was then determined by estimating the amount of phosphate extracted by boiling with a solution of 1.0*N*-NaOH for 10 minutes. The soluble silicates were first removed from the filtrate by the usual method. The colorimetric method of Peech and English (*Soil Sci.*, 1944, **57**, 169) was followed for the determination of phosphate, but instead of visual comparison, the colour was matched in the Klett-Summerson photoelectric colorimeter. The p.a.c. estimated in this way amounted to 17.8 m.e. PO_4^{3-} per 100 g. kaolinite.

The anion-exchange resin (Amberlite IR-410), supplied by Messrs. Rohm & Haas, was in the chloride form. From this the hydroxide, fluoride, oxalate and citrate forms were prepared by leaching with $M/5$ solutions of sodium hydroxide, fluoride, oxalate and citrate respectively till the leachate was free from chloride. After washing off the adhering ions, the resins were dried in an electric oven at 105° and kept in desiccators.

The anion-exchange capacity of the OH-resin was determined by treating it with an excess of standard acid and back-titrating the excess. The value so determined was 458 m.e./100 g., and was taken to be the same for the fluoride, citrate and oxalate resins.

Measurement of Exchangeable Phosphate.—The experimental procedure consisted in placing the phosphatised kaolinite suspension in a bottle and dipping into it a cellophane bag containing a known weight of slightly moistened anionic resin. The amounts of the phosphatised kaolinite as well as of the resin were varied. The amounts of resin, for instance, in each set of experiments were so taken that these corresponded to 1.0, 1.5, and 2.0 and 3.0 times the symmetry concentration.

After allowing the system to remain in this condition for 7 days, the bag containing the resin was taken out of the clay suspension. The amount of phosphate present in the clay after exchange was then determined by the method of Peech and English (*loc. cit.*). The phosphate so determined is expressed in m.e. of PO_4^{3-} ions per 100 g. of phosphatised kaolinite. The results are recorded in Tables I to IV.

TABLE I

Reaction between OH-*resin and phosphatised kaolinite.*

Total PO_4 = 17.8 m.e. p_H = 6.0.

	Amount of resin corresponding to	M. e. of PO_4-ion exchanged for OH-ions/100 g. 1.033% clay.	2.066% clay.	4.132% clay.
1.	1.0 S.	6.6	8.7	Nil
2.	1.5 S.	7.7	9.5	4.5
3.	2.0 S.	...	9.6	7.0
4.	3.0 S.	17.8	13.3	10.4

TABLE II

Reaction between oxalate-resin and phosphatised kaolinite.

Total PO_4 = 17.8 m.e. p_H = 6.0.

Amount of resin corresponding to		M. e. of PO_4-ions exchanged for oxalate-ions/100 g. 1.033% clay.	2.066% clay.	4.132% clay
1.	1.0 S.	1.7	2.2	Nil
2.	1.5 S.	2.4	2.2	Nil
3.	2.0 S.	3.2	2.5	Nil
4.	3.0 S.	5.2	2.5	1.8

TABLE III

Reaction between citrate-resin and phosphatised kaolinite.

Total PO_4 = 17.8 m.e. p_H = 6.0.

Amount of resin corresponding to		M. e. of PO_4-ions exchanged for citrate-ions/100 g. 1.033% clay.	2.066% clay.	4.132% clay.
1.	1.0 S.	10.9	3.3	3.6
2.	1.5 S.	11.9	7.7	6.1
3.	2.0 S.	15.7	9.9	10.8
4.	3.0 S.	17.8	13.6	10.8

TABLE IV

Reaction between F-resin and phosphatised kaolinite.

Total PO_4 = 17.8 m.e. p_H = 6.0.

Amount of resin corresponding to		M. e. of PO_4-ions exchanged for F'-ions/100 g. 1.033% clay.	2.066% clay.	4.132% clay.
1.	1.0 S.	Nil	Nil	Nil
2.	1.5 S.	Nil	Nil	Nil
3.	2.0 S.	Nil	0.2	Nil
4.	3.0 S.	0.6	1.7	1.3

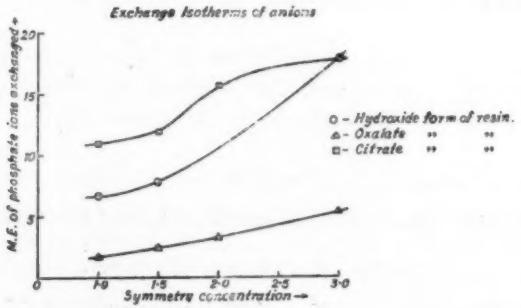
DISCUSSION

From the above data it is evident that extent of replacement of phosphate depends on the nature of the exchanging anion associated with the resin. Fluoride ions are apparently unable to replace phosphate from kaolinite (except a very small amount at high symmetry concentration) under the conditions of the experiment. It may be noted that a mixture of NH_4F and HCl at p_H 3.0 is capable of completely releasing adsorbed phosphate and this procedure is recommended for the determination of available phosphorus in soil (Bray, Bull. Ag. No.1021, Agr. Expt. Sta., Illinois, 1942). The p_H of the phosphatised clay in the present experiment is about 6.0 and the high p_H may be responsible for the observed discrepancy.

Hydroxyl, oxalate and citrate ions, on the other hand, can replace varying amounts of phosphates from phosphatised kaolinite according to the respective capacity of each ; the amounts of phosphate exchanged generally decrease to a small extent with the concentration of the phosphatised kaolinite. It appears that from 4% suspension, the oxalate ions are almost incapable of releasing the phosphate. In the case of concentrated clays, longer time is usually allowed for equilibrium.

Exchange of phosphate for the citrate ions increases with the quantity of citrate resin, *i.e.*, symmetry concentration, but the amount of exchange decreases with increasing concentration of the suspension. It appears therefore that the availability of the phosphate ions is reduced as the clay becomes more and more concentrated. Activity measurements have similarly shown that the extractability or availability of cations is reduced at high concentrations of clay (Chatterjee, this *Journal*, 1956, **33**, 399) due possibly to the overlapping of double layers and consequent "immobilisation" of the ions in the double layer. A similar state of affairs may be envisaged in the case of phosphate availability.

FIG. 1



The three anion-exchange isotherms (Fig. 1), drawn for the least concentrated system, show their difference from the base-exchange isotherms, which are usually concave to the concentration.

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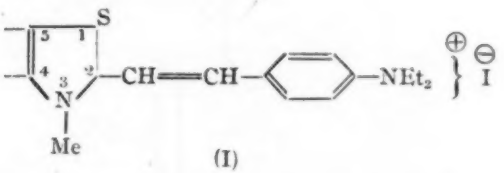
SYNTHESIS OF CYANINE DYES BY THE CONDENSATION OF *p*-DIETHYLAMINOBENZALDEHYDE WITH APPROPRIATE HETEROCYCLIC COMPOUNDS. PART VII

By M. Q. Doja and J. C. Banerjee

Six new cyanine dyes have been prepared by condensing *p*-diethylaminobenzaldehyde with the methiodides of 2-methyl-(4-*p*-tolyl-, 4-*p*-chlorophenyl-, 4-*p*-bromophenyl-, 4-*p*-iodophenyl-, 4:5-diphenyl)- and 2:5-dimethyl-4 phenyl- thiazoles, and their optical and other properties have been examined. Results of previous communications have been collated and it has pointed out that with regard to the extra-sensitisation conferred, substitution at the 5-position of the thiazole nucleus is more effective than that at the 4-position, while the substituents at the 4-position fall in the order: (*p*)I.C_6H_4- < (*p*)Br.C_6H_4- < (*p*) Cl.C_6H_4- > (*p*) CH_3.C_6H_4- > C_6H_5- > CH_3-.

The inclusion of thiazole nuclei, simple or condensed, in the auxochromatic chain of a cyanine dye has yielded a large number of powerful sensitisers. Even as the character of the heterocyclic nuclei, forming part of the auxochromatic chain of the cyanine dyes, plays a vital role in conferring extra-sensitising property to the dye, the complexity of the nuclei and the length of the conjugated chain separating them are of no less importance.

It will be at once seen that if the nature of the heterocyclic rings and the length of the conjugated chain separating them be kept the same, the complexity of the nuclei (determined by the position and the nature of substituents therein) becomes the sole determinant of the extra-sensitivity of the dyes. It was thus of interest to study the effect of position and the nature of substituents in the 4- and 5- positions of 2-*p*-diethylaminostyrylthiazole methiodide (I).

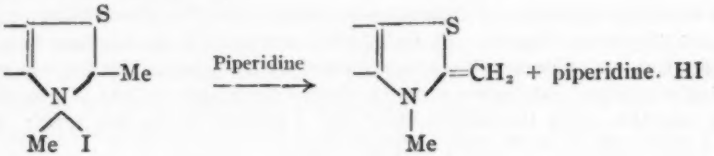


(I)

Some of the results of this investigation have already been reported (Parts II and III, Doja and Banerjee, this *Journal*, 1946, **23**, 217; 1949, **26**, 374). Six new dyes (I, B, G, A, D and E) have now been prepared by condensing *p*-diethylaminobenzaldehyde with the methiodides of 2-methyl-(4-*p*-tolyl-, 4-*p*-chlorophenyl-, 4-*p*-bromophenyl-, 4-iodophenyl-, 4:5-diphenyl)- and 2:5-dimethyl-4-phenyl-thiazoles. The methodides have in all cases been prepared by heating the base in sealed tubes on a water-bath for 24 hours, the methiodides with salts being subsequently recrystallised from suitable solvents. The condensation of the methiodides with *p*-diethylaminobenzaldehyde has been effected by refluxing the constituents in absolute alcohol using piperidine as a catalyst. The dyes (G), (A) and (E) crystallised out of the solution on cooling, while the dye (I) was precipited by adding dry ether to the cooled alcoholic solution. The dyes (B) and (D), which could not be obtained by either of the two methods, were obtained in a crystalline form

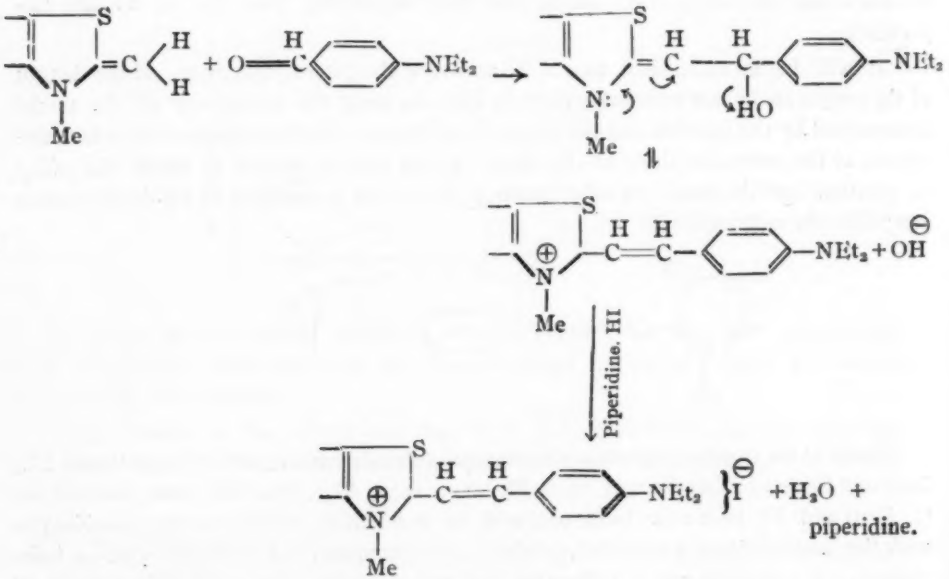
by adopting the procedure recorded in the experimental. The dye (D) could, however, also be crystallised by suddenly chilling the alcoholic solution in a freezing mixture.

The mechanism of the reaction involved in the formation of these dyes is probably dependent on the passage of the active methyl group of the quaternised base to the methylene group (IIa ⟶ IIb), the required elimination of HI being facilitated by the presence of the basic condensing agent, piperidine, as postulated by Mills and Raper (*J. Chem. Soc.*, 1925, **127**, 2466).



(IIa) (IIb)

The methylinic hydrogen atom of the postulated intermediate may then condense with the carbonyl group of the aldehyde to form the dye with the elimination of water, thus*:



The intensities of colour of the dyes in rectified spirit solutions (1 : 10,000) have been determined by a Duboscq colorimeter and the relative intensities are shown in Table I. The findings with respect to the dyes (A) and (E) are shown in parenthesis as these two are mauve in solution, while the rest are in shades of pinkish brown.

* Recently, however, some doubts have been expressed by Brooker and White (*Chem. Abs.*, 1950, **44**, 7173; *Phot. Abs.*, 1950, III, 149; U.S.P. 2494032/1950) as to the validity of the Mills-Raper mechanism in the formation of these types of dyes, as indicated above.

TABLE I

Dye.	Reflex.	Colorimeter reading.	N/100-HCl reqd.	Pleochroism. Colour of light at one position of polariser.	Colour of light at ⊥ to the polariser.	Extra-sensitisation. Range.	Max.	Frequency of max. absorption × 10^{14}.
B	Weak green gold	20	6.0c.c.	Colorless	Dark steel blue	4800-6400Å	5620Å	62500
D	Very weak red	16.2	6.5	Rose	Claret	4840-6320	5620	62500
G	Strong golden yellow	16.0	6.5	Bottle-green	Yellowish brown	4800-6500	5500 (faint)	61983
I	Light blue	10.3	8.0	Red	Weak orange	4850-6300	5640	63291
A	Old gold	5.5	35.1	Greenish yellow	Reddish brown	5200-6540	6000	59289
E	Strong bluish red	10	6.5	Bluish red	Deep orange	4940-6540	5800	59524

The colour of the dye solutions is reversibly discharged by the addition of mineral acids. The relative resistances to decolorisation, as determined by titrating 2 c.c. of 1 : 50,000 solutions of the dyes in rectified spirit with $N/100$-HCl, are shown in Table I.

The dyes produce shades on cotton, silk and wool when dyed from alcoholic solutions, as shown in Table II, but the shades produced are fugitive to sunlight and are not fast to washing.

TABLE II

Dye.	Colour and shade on Cotton.	Silk.	Wool.
B	Light pinkish rose	Light orange-red	Light rose
D	Brownish pink	Brown	Brown
G	Orange-red	Orange-red	Brownish rose
I	Rose	Brownish rose	Light reddish brown
A	Mauve	Mauve	Bluish mauve
E	Mauve	Bluish mauve	Light bluish mauve

The fluorescence of weak alcoholic solutions (1/50,000) of these dyes (cf. Doja, this *Joural*, 1940, **17**, 348) is given in Table III.

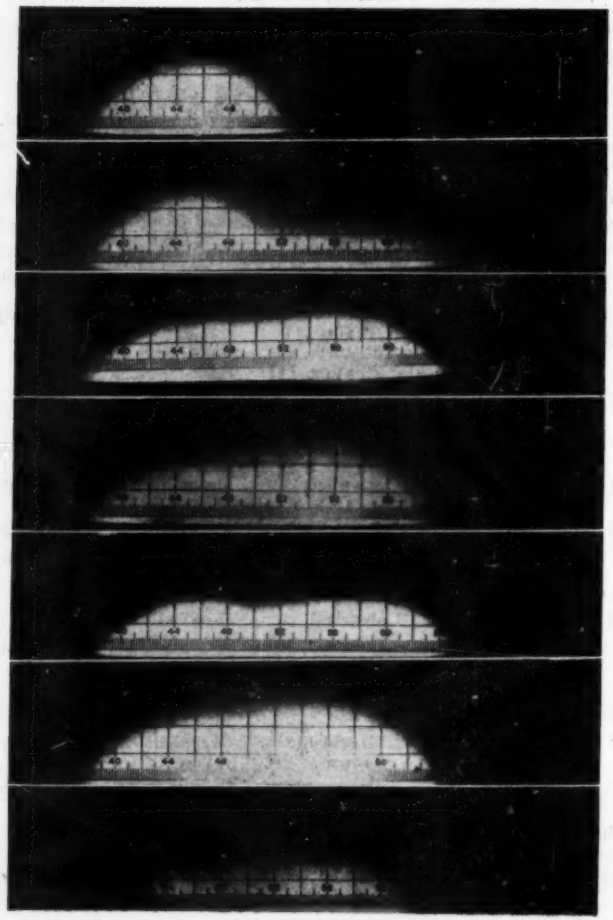
TABLE III

Wallace colour filter No.	Colour of fluorescent beam seen at right angle to the incident beam. B.	D.	G.	I.	A.	E.
1	Light absorbed	Light absorbed	Light absorbed	Light absorbed	Light absorbed	Weak red
2	Light absorbed	Brown-red	Light absorbed	Light absorbed	Light absorbed	Greenish yellow
3	Weak yellow	Brownish yellow	Orange-yellow	Pale yellow	Brownish yellow	Weak red
4	Light absorbed	Orange-yellow	Light absorbed	Light absorbed	Weak brown	Dull yellow
5	Orange-yellow	Brownish yellow	Lemon-yellow	Weak brown-yellow	Yellowish brown	Dull yellow
6	Orange-yellow	Brownish yellow	Dirty yellow	Faint brownish yellow	Lemon-yellow	Weak red
7	Greenish brown	Greenish brown	Greenish brown	Greenish yellow	Greenish yellow	Yellow
8	Brownish yellow	Light absorbed	Orange-yellow	Orange-yellow	Brownish orange	Yellow
9	Brownish yellow	Light absorbed	Orange-yellow	Orange-yellow	Carrot yellow	Dull orange. yellow
10	Orange-yellow	Carrot yellow	Bright yellow	Yellow	Brownish yellow	Dull orange-yellow

A noteworthy phenomenon, also observed in previous cases (Doja and Banerjee, *loc. cit.*), is that the acetic acid solutions of these dyes deepen in colour on warming, the original intensity of colour being regained on cooling. The effect is more pronounced in aqueous acetic acid solutions. It is likely that the state of molecular aggregation of the dyes (Sheppard, *Rev. Mod. Phys.*, 1942, **14**, 303 ; *Science*, 1941, **93**, 42; Jelley, *Nature*, 1936, **138** 1009 ; 1937, **139**, 631 ; Leermakers *et al.*, *J. Chem. Phys.*, 1937, **5**, 878 ; Dickinson, *Phot. J.*, 1948, **88B**, 97) has something to do with this peculiar phenomenon. The aggregated molecules in acetic acid solution, perhaps, disintegrate on warming, producing deeper colour, while the return to the aggregated state on cooling causes a diminution in colour intensity.

Some of the other properties of the dyes are shown in Table I, and the sensitisation spectrographs are shown in Fig. 1. For the sake of comparison, the sensitisation spectrograph of an unbathed process plate is appended in Fig. 1.

FIG. 1



For a complete study of the effect of substitution on sensitisation, the results of previous communications (Doja and Banerjee, *loc. cit.*) have been collated here. The sensitisation spectrographs of the dyes 2-*p*-diethylaminostryryl-5-methylthiazole methiodide (Dye Q) and 2-*p*-diethylaminostyryl-4 : 5-dimethylthiazole methiodide (Dye R), reported in Part III (*loc. cit.*), were retaken with a slight improvement in the technique with the following results :

Dye.	Extra-sensitisation. Range.	Max.	Frequencies of max. abs. × 10^{10}.
Q	5000-6240Å	Nil	61225
R	4750-6290	5200-5800Å	65934

It will be seen from Table I and also from Parts II and III (*loc. cit.*) that substitution at the 4-position of the thiazole nucleus has profoundly affected the extra-sensitisation of the dyes, the range varying with the nature of the substituent group. The groups at 4-position imparting extra-sensitisation may be arranged in the following order :

While the 4-methyl dye sensitises up to 6000 Å, the 4-*p*-iodophenyl dye extends the extra-sensitisation up to 6540Å. The substitution at the 5-position seems to have a greater effect than that in the 4-posftion, the 5-methyl dye sensitising up to 6240Å. Di-substitution, as expected, confers still greater sensitisation than either of the corresponding mono-substituted dyes.

The *p* diethyl dyes, reported here, are better sensitisers than their corresponding *p*-dimethyl analogues, as will be seen from Table IV, the sensitisation data having been collected from relevant publications.

TABLE IV

Methiodide of 2-*p*-dimethylaminostyryl-thiazole	Corresponding diethyl dye.	Sensitisation. Range.	Max.	Reference.
-4-*p*-tolyl-	I	6250Å	5500Å	Banerji and Banerjee this *Journal*, 1954, **31**, 509.
-4-*p* chlorophenyl-	B	6250	5600	Do.
-4-*p*-bromophenyl-	G	6250	5800	Do.
-4-*p*-iodophenyl-	A	6200	5600	Do.
-4-phenyl-5-methyl-	D	6250	5800	Smith, *J. C. S.*, 1923, 2288.
-4 :5-diphenyl- „	R	6250	5600	Do.

I : 2-*p*-Diethylaminostyryl-4-*p*-tolylthiazole methiodide
B : „ „ „ chlorophenylthiazole methiodide
G : „ „ „ bromophenyl „ „
A : „ „ „ iodophenyl „ „
D : „ „ 4-phenyl-5-methylthiazole „
R : „ „ 4 :5-diphenylthiazole „

Experimental

2-p-*Diethylaminostyryl*-4-p *tolylthiazole Methiodide*.—2-Methyl-4-*p*-tolylthiazole methiodide (Banerji and Banerjee, *loc. cit.*) (0.7 g.), *p*-diethylaminobenzaldehyde (0.4 g.), absolute alcohol (10 c.c.) and piperidine (4 drops) were refluxed for 12 hours. The dye was precipitated by adding dry ether to the cold reaction mixture (yield 60%) and was recrystallised from methyl alcohol as dark reddish blue, broken needles, m.p. 184°. (Found: N, 5.8; I, 25.8. $C_{23}H_{27}N_2IS$ requires: N, 5.7; I, 25.9%).

2-p-*Diethylaminostyryl*-4-p-*chlorophenylthiazole Methiodide*.—2-Methyl-4-*p*-chlorophenylthiazole methiodide (Banerji and Banerjee, *loc. cit.*) (0.6 g.), *p*-diethylaminobenzaldehyde (0.4 g.), absolute alcohol (10 c.c.) and piperidine (4 drops) were refluxed for 24 hours but the dye did not separate. The whole mass was then heated on the steam-bath to drive off as much alcohol as possible. The residue was washed with ether to remove any unchanged aldehyde. The sticky residue was then dissolved in the least quantity of hot glacial acetic acid from which the dye crystallised out on standing for 72 hours, yield 30%. It was recrystallised from methyl alcohol as felt-green needle clusters, m.p. 160°. (Found: N, 5.6; Cl+I, 31.7. $C_{23}H_{24}N_2ClIS$ requires N, 5.5; Cl+I), 31.8%).

2-p-*Diethylaminostyryl*-4-p-*bromophenylthiazole Methiodide*.— By refluxing a mixture of 2-methyl-4-*p*-bromophenylthiazole methiodide (Banerji and Banerjee, *loc. cit.*), *p*-diethylaminobenzaldehyde (0.2 g.), absolute alcohol (10 c.c.) and piperidine (2 drops) for 18 hours, the dye (17%) separated from the solution. It was recrystallised from methyl alcohol as dark greenish yellow crystals, m.p. 198°. (Found: N, 5.1; Br+I, 37.3. $C_{23}H_{24}N_2BrIS$ requires N, 5.0; Br+I, 37.4 %).

2-p-*Diethylaminostyryl*-4-p-*iodophenylthiazole Methiodide*.—When 2-methyl-4-*p*-iodophenylthiazole methiodide (Banerji and Banerjee, *loc. cit.*) (0.9 g.), *p*-diethylaminobenzaldehyde (0.4 g.), absolute alcohol (10 c.c.) and piperidine (4 drops) were refluxed for 2 hours, the dye (37.5 %) separated. It was recrystallised from methyl alcohol as golden green, stunted needles, m.p. 211°. (Found: N, 4.7; I, 42.0. $C_{23}H_{24}N_2I_2S$ requires N, 4.7; I, 42.2 %).

4-*Phenyl*-2:5-*dimethylthiazole Methiodide*.—By heating 4-phenyl-2:5-dimethylthiazole (Smith, *loc. cit.*) and methyl iodide (1:1.5 molar) in a sealed tube on a steam-bath for 48 hours, the salt was obtained and was recystallised from absolute alcohol, m.p. 181°. Smith reported the m.p. of the anhydrous salt as 171°. (Found: N, 4.2; I, 38.4. Calc. for $C_{12}H_{14}NIS$: N, 4.2; I, 38.2 %).

2-p-*Diethylaminostyryl*-4-*phenyl*-5-*methylthiazole Methiodide*.—The dye was prepared by the following two methods:

(*a*). A mixture of the above methiodide (1.0 g.), *p*-diethylaminobenzaldehyde (0.2 g.), absolute alcohol (10 c.c.) and 4 drops of piperidine was refluxed for 5 hours but the dye did not separate on cooling. A crop of crystals were, however, obtained by suddenly chilling the reaction mixture, yield 65%. The dye was recrystallised from methyl alcohol as maroon-red needles, m.p. 201°.

(*b*). The dye was obtained by adopting the procedure as in the case of dye B. Recrystllised from methyl alcohol, it had m.p. 200°.

Analyses of the two samples gave the following results. Sample from (*a*): Found: N, 5.8; I, 25.8. Sample from (*b*): Found: N, 5.8; I, 25.8. $C_{23}H_{27}N_2IS$ requires N, 5.7; I, 25.9%.

2-p-*Diethylaminostyryl-4:5-diphenylthiazole Methiodide.*—By refluxing 2-methyl-4:5-diphenylthiazole methiodide (Smith, *loc. cit.*) (0.4 g.), *p*-diethylaminobenzaldehyde (0.2 g.), absolute alcohol (5 c.c.) and piperidine (2 drops) for 2 hours, the dye separated (37%). It was recrystallised from methyl alcohol as blunt ruby-red needles, m.p. 218°. (Found: N, 5.0; I, 23.4. $C_{28}H_{29}N_2IS$ requires N, 5.1; I, 23.1 %).

The authors wish to record their grateful thanks to Professor L. M. Chatterjee, Science College, Patna, for his kind help in recording the absorption and sensitisation spectrographs.

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PHASE STUDY IN THE SYSTEM $Pb(NO_3)_2-KNO_2-H_2O$

By. D. G. Vartak and M. B. Kabadi

During the phase study of the system $Pb(NO_3)_2$-KNO_2-H_2O different crops of crystals, separated at different stages of crystallisation, have been analysed. Amongst these are found crystals respectively of the compositions : (*i*) $4KNO_2.Pb(NO_3)_2$, (*ii*) $2KNO_2.Pb(NO_3)_2$ and (*iii*) $KNO_2.Pb(NO_3)_2$, in agreement with the inferences drawn in the previous communication (this *Journal*, 1955, **32**, 351).

Vartak and Kabadi (this *Journal*, 1955, **32**, 351) have shown from the study of conductivity and the thermometric titrations the existence of the molecular compounds: (*i*) $4KNO_2.Pb(NO_3)_2$, (*ii*) $2KNO_2.Pb(NO_3)_2$ and (*iii*) $KNO_2.Pb(NO_3)_2$ in solutions containing potassium nitrite and lead nitrate in different molar concentrations. The present paper describes the phase study of the system containing these two constituents in various molar proportions.

Experimental

The different mixtures containing lead nitrate and potassium nitrite respectively in molar proportions 1 : 3, 1 : 2, 1 : 1, 2 : 1 and 3 : 1 were evaporated at room temperature over P_2O_5 in vacuum desiccators. These were evacuated from time to time with Cenco-hyvac pump. At different stages of the process of crystallisation, crops of crystals separated out. After washing them with 80% alcohol and drying over calcium chloride to constant weight, each crop and the corresponding mother-liquor were analysed for Pb^{2+}, K^+, NO_2^- and NO_3^- respectively. The results are recorded in Table I.

TABLE I

S. No.	Composition of the mother-liquor.	Percentage composition of the crop separated. K.	Pb.	NO_2.	NO_3.	H_2O.	Empirical composition / Molecular composition	Nature. Colour.	Stability.
1.	(i) $3KNO_2$+ $Pb(NO_3)_2$	15.51	41.19	27.44	12.32	3.579	$\frac{K_2Pb(NO_2)_3(NO_3).H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2H_2O.4KNO_2}$	Orange-red.	Stable in dry air. Absorb moisture from atmosphere very rapidly.
	(ii) $7KNO_2$+ $Pb(NO_3)_2$	15.51	41.19	27.44	12.32	3.579	$\frac{K_2Pb(NO_2)_3(NO_3).H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2H_2O.4KNO_2}$	Do	Do
	(iii) $4KNO_2$+ $Pb(NO_3)_2$	22.64	30.04	26.71	18.00	2.61	$\frac{K_4Pb(NO_2)_4(NO_3)_2.H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3.2H_2O.6KNO_2}$	Yellowish orange	Stable in dry air. Absorb moisture from atmosphere slowly.
2.	(i) $2KNO_2$+ $Pb(NO_3)_2$	15.51	41.19	27.44	12.32	3.579	$\frac{K_2Pb(NO_2)_3(NO_3).H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2H_2O.4KNO_2}$	Orange-red	Stable in dry air. Absorb moisture from atmosphere very rapidly.
	(ii) K_8Pb_5– $(NO_2)_7(NO_3)_3$	15.51	41.19	27.44	12.32	3.579	$\frac{K_2Pb(NO_2)_3(NO_3).H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2H_2O.4KNO_2}$	Do	Do
	(iii) $2KNO_2$+ $Pb(NO_3)_2$	15.03	39.88	17.72	23.89	3.486	$\frac{K_2Pb(NO_2)_2(NO_3)_2.H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3.2H_2O.2KNO_2}$	Yellowish orange	Stable at room temperature in dry atmosphere. Absorb moisture slowly from atmosphere.
3.	(i) KNO_2+ $Pb(NO_3)_2$	15.03	39.87	17.72	23.89	3.49	$\frac{K_2Pb(NO_2)_2(NO_3)_2.H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3.2H_2O.2KNO_2}$	Do	Do
	(ii) $6KNO_2$+ $7Pb(NO_3)_2$	9.59	50.20	9.16	33.10	...	$\frac{K_8Pb_5(NO_2)_4(NO_3)_{11}}{2[Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3].KNO_3.Pb(NO_3)_2}$	Lemon-yellow	Stable at room temperature Practically unaffected by atmospheric moisture.

TABLE I (contd.)

S. No.	Composition of the mother-liquor.	Percentage composition of the crop separated. K.	Pb.	NO_2.	NO_3.	H_2O.	Empiricial composition / Molecular composition'	Nature. Colour.	Stability.
3.	(iii) $K_4Pb_5(NO_2)_6(NO_3)_8$	7.874	52.24	13.93	25.03	0.926	$\frac{K_4Pb_5(NO_2)_6(NO_3)_8.H_2O}{2[Pb(NO_2).Pb(NO_3)_2\ 2KNO_3.2H_2O].Pb(NO_2)_2}$	Deep yellow crystals	Stable at room temperature in dry atmosphere. Absorb moisture from the atmosphere slowly.
4.	(i) $KNO_2+2Pb(NO_3)_2$	...	62.55	...	37.45	...	$\frac{Pb(NO_3)_2}{Pb(NO_3)_2}$	...	...
	(ii) $2KNO_2+3Pb(NO_3)_2$	4 233	56.15	4.992	33.62	0.984	$\frac{K_2Pb_5(NO_2)_2(NO_3)_{10}.H_2O}{[Pb(NO_2)_2.Pb(NO_3)_2\ 2KNO_3.H_2O].3Pb(NO_3)_2}$	Lemon-yellow	Stable at room temperature. Practically unaffected by the atmospheric moisture.
	(iii) $KNO_2+Pb(NO_3)_2$	8.97	47.61	10 58	28.52	4 32	$\frac{KPb(NO_2)(NO_3)_2.H_2O}{Pb(NO_2)_2.Pb(NO_3)_2\ 2KNO_3.2H_2O}$	Yellow	Stable at room temperature.
5.	(i) $KNO_2+3Pb(NO_3)_2$	...	62.55	...	37.45	...	$\frac{Pb(NO_3)_2}{Pb(NO_3)_2}$	...	...
	(ii) $3KNO_2+5Pb(NO_3)_2$	1.416	60.28	1.671	35.98	0.653	$\frac{KPb_5(NO_2)(NO_3)_{16}.H_2O}{[Pb(NO_2)_2\ Pb(NO_3)_2.2KNO_3.2H_2O].14Pb(NO_3)_2}$	Lemon-yellow	Stable at room temperature. Practically unaffected by atmospheric moisture.
	(iii) $3KNO_2+2Pb(NO_3)_2$	12.57	44.28	14.78	26.52	1.87	$\frac{K_3Pb_3(NO_2)_3(NO_3)_4.H_2O}{Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3.H_2O.KNO_2}$	Yellow	Stable at room temperature in dry atmosphere. Absorb moisture from the atmosphere slowly.

TABLE I (contd.)

S. No.	Comp. of the mother-liquor.	Mol. comp. of the crystals separated
1.	(i) $3KNO_2+Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.2KNO_2.H_2O$
	(ii) $7KNO_2+Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.2KNO_2.H_2O$
	(iii) $4KNO_2+Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.KNO_3(3KNO_2).H_2O$
2.	(i) $2KNO_2+Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.2KNO_2.H_2O$
	(ii) $K_4Pb_3(NO_2)_7(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.2KNO_2.H_2O$
	(iii) $2KNO_2+Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.KNO_2.KNO_2.H_2O$
3.	(i) $KNO_2+Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.KNO_3.KNO_2.H_2O$
	(ii) $6KNO_2+7Pb(NO_3)_2$	$4(Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.KNO_3).KNO_3.Pb(NO_3)_2$
	(iii) $K_4Pb_3(NO_2)_6(NO_3)_2$	$2(Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.2KNO_2).H_2O+3Pb(NO_3)_2$
4.	(i) $KNO_2+2Pb(NO_2)_2$	$Pb(NO_3)_2$
	(ii) $2KNO_2+3Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.2KNO_3.KNO_2.H_2O+4Pb(NO_3)_2$
	(iii) $KNO_2+Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.KNO_3.H_2O$
5.	(i) $KNO_2+3Pb(NO_3)_2$	$Pb(NO_3)_2$
	(ii) $3KNO_2+5Pb(NO_3)_2$	$Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.KNO_3.H_2O+7Pb(NO_3)_2$
	(iii) $3KNO_2+2Pb(NO_3)_2$	$2(Pb<\begin{matrix}NO_2\\NO_3\end{matrix}.KNO_3)KNO_3.H_2O$

Discussion

In column four of Table I are shown the empirical compositions of the crystals, separated in every stage. The closer inspection of this column shows the presence of the crystals having the molecular composition as shown below :

Soln. No.	Crop No.	Comp. of the crystals.	Molar ratio.
1	3	$4KNO_2.Pb(NO_3)_2.H_2O$	4 : 1
2	2	$2KNO_2.Pb(NO_3)_2.H_2O$	2 : 1
3	1	$2KNO_2.Pb(NO_3)_2.H_2O$	2 : 1
4	3	$KNO_3.Pb(NO_3)_2.H_2O$	1 : 1

These results appear to be in agreement with the findings of conductometric and thermometric study of similar solutions, made earlier by the authors (*loc. cit.*).

During similar study of mixtures containing lead nitrate and lead nitrite (to be published later) evidence has been found of the existence of the compound of composition $Pb(NO_2)_2.Pb(NO_3)_2$. If mixtures in the present investigation are assumed to contain such a compound, the composition of the three compounds, mentioned above, may be expressed in the following manner :

(*i*) $4KNO_2.Pb(NO_3)_2.H_2O$ ... $Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3.2H_2O.6KNO_2$.

(*ii*) $2KNO_2.Pb(NO_3)_2.H_2O$ ... $Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3.2H_2O.2KNO_2$.

(*iii*) $KNO_2\ Pb(NO_3)_2.H_2O$ ... $Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3.2H_2O$.

It is thus shown that these compounds are the mixed crystals containing $Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3$ as a chief constituent. The study of the stability of these compounds and their behaviour regarding the absorption of moisture from atmosphere, which is shown in the last column of Table I, points out some interesting results. The crop $Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3$ tends to absorb miosture very slowly from the atmosphere. The mixed crystals containing this compound and potassium nitrite do not appear to be so stable. Actually it has been found that the stability of the compound decreases as the number of potassium nitrite molecules present therein increases. The mixed crystals containing lead nitrate are found to be more stable and do not absorb any moisture. The crop (*ii*) of the solution (3) has the composition $K_5Pb_5(NO_2)_4(NO_3)_{11}$. The molecular composition of the crop may be expressed as $2[Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3].KNO_3.Pb(NO_3)_2$. The reason for assigning the composition in the bracket has already been given above. Nayar and Pande (*Proc. Ind. Acad. Sci.*, 1948, **27A**, 284 ; 1949, **30A**, 251) have inferred the existence of the compound, $KNO_3.Pb(NO_3)_2$, in solution from the study of certain physical properties of the solutions containing lead nitrate and potassium nitrate. It thus appears that these crystals are the mixed crystals containing $2[Pb(NO_2)_2.Pb(NO_3)_2.2KNO_3]$ and $KNO_3.Pb(NO_3)_2$. The closer examination of Table I shows that these crystals separated out from the mother-liquor containing an excess of lead nitrate. Potassium nitrate is presumed to have been formed during the reaction.

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SEARCH FOR NEW AMOEBACIDES. PART I

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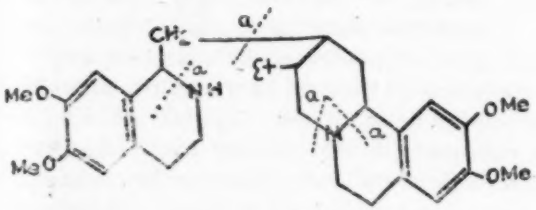
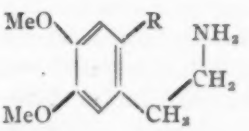
β-(2-Alkyl-4:5-dimethoxyphenyl)-ethylamines have been synthesised through seven steps: Veratrole → 4-acylveratrole → 4-alkylveratrole → 2-alkyl-4:5-dimethoxybenzaldehyde → 2-alkyl-4:5-dimethoxycinnamic acid → β-(alkyl-4:5-dimethoxyphenyl)-propionic acid → β-(2-alkyl-4:5-dimethoxyphenyl)-propionamide → β-(2-alkyl-4:5-dimethoxyphenyl)-ethylamine.

The mode of action of emetine in amoebiasis has not been fully established. It is considered that emetine undergoes some degradation in the system, and on this basis Child and Pyman (*J. Chem. Soc.*, 1929, 2010), Pyman (*Chem. & Ind.*, 1937, **56**, 789), Goodwin *et al.* (*Brit. J. Pharmacol.*, 1948, **3**, 44), Goodson *et al.* (*ibid.*, 1948, **3**, 49, 62), Hall *et al.* (*J. Chem. Soc.*, 1950, 1842; 1952, 149) and Mahboob and Dhar (*J. Sci. Ind. Res.*, 1955, **14B**, 1) have synthesised several diamines, which may be considered as cleavage products of the emetine molecule. None of them have proved to be superior to emetine *in vivo*.

If the opening of the emetine molecule (I) is considered along the dotted lines 'a', the molecule transforms to a compound of the type (II). It has been considered worthwhile to synthesise compounds of this type with various alkyl group substitution at R, to examine their amoebacidal activity.



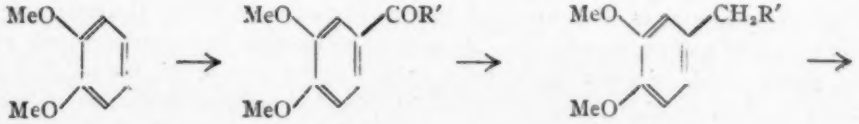
(I)



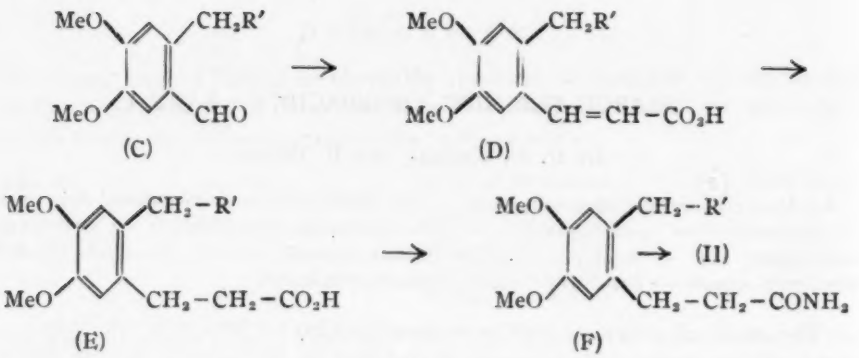
(II)

Attempts to alkylate or acylate acylated 3:4-dimethoxyphenylethylamine by the Friedel-Crafts reaction proved abortive, although condensation was attempted in different solvents like ether, carbon disulphide and nitrobenzene, using anhydrous aluminium chloride as a condensing agent.

Synthesis of compounds of the type (II) has now been effected according to the following scheme :



(A) (B)



Acetoveratrone was prepared in good yield by Pictet and Gams (*Ber.*, 1909, **42**, 2947) by condensing veratrole with acetyl chloride in presence of anhydrous aluminium chloride. The same method has been found to afford poor yields of acylveratroles (A) with higher acid chlorides. It has been found that if the above condensation is effected in presence of anhydrous zinc chloride at the boiling temperature of carbon disulphide, yields improve appreciably and the formation of tarry matter also decreases. Barger and Silverschmidt (*J. Chem. Soc.*, 1928, 2924) reduced acetoveratrone (A : R′ = Me) by the Clemmensen method in good yield. Following the same procedure, higher acylveratroles have been reduced to alkylveratroles (B) in 60 to 77% yield. Perkin and Weizman (*J. Chem. Soc.*, 1906, **89**, 1648) prepared 2-methyl-4 : 5-dimethoxybenzaldehyde in 32% yield. Barger and Silverschmidt (*loc. cit.*) synthesised 2-ethyl-4 : 5-dimethoxybenzaldehyde, but no mention of yield was made. Both the aldehydes were prepared by the above workers according to Gattermann's aldehyde synthesis with the use of hydrogen cyanide. Aldehydes of the type (C) have now been prepared according to Adams' modified Gattermann synthesis (*J. Amer. Chem. Soc.*, 1924, **46**, 1518) in 29 to 71% yields. Preparation of the compounds of the type (D) has been effected according to Knoevenagel's modified method of the Perkin reaction (*Ber.*, 1898, **31**, 2598). This method is essentially the same as was applied by Robinson and Shinoda (*J. Chem. Soc.*, 1925, **127**, 1977) for the preparation of 3 : 4-dimethoxycinnamic acid from veratraldehyde. Reduction of these cinnamic acids (D) by excess of sodium amalgam in the usual manner has yielded the corresponding dihydrocinnamic acids (E) in 75 to 88% yields. Haworth and Perkin (*J. Chem. Soc.*, 1926, 1769) prepared β-3 : 4-dimethoxyphenylpropionamide in 30% yield by passing a stream of dry ammonia gas through the corresponding acid at 210° for two hours. By the same method β-2-alkyl-4 : 5-dimethoxyphenyl-propionamides (F) have been prepared in good yields. Conversion of the above amides (F) to β-(2-alkyl-4 : 5-dimethoxyphenyl)-ethylamines (II) has been effected in poor yields by the Hofmann reaction with the use of sodium hypochlorite. A mixture of bromine and caustic potash afforded poorer yield. Sodium hypochlorite yielded only a trace of (II, R = n-C_6H_{13}) from the amide (F : R′ = n-C_5H_{11}) and in this case bromine and sodium methoxide in methanolic solution (Jeffreys, *Amer. Chem. J.*, 1899, **22**, 14) was successfully used.

*EXPERIMENTAL

2-Methyl-4 : 5-dimethoxybenzaldehyde (C : R′=H).—To a mixture of homoveratrole (60 g.), zinc chloride (60 g.) and dry benzene (220 c.c.), taken in a three-necked flask fitted with a mercury seal stirrer and a reflux condenser, cooled in an ice bath, was passed dry HCl gas for 1 hour. Powdered $AlCl_3$ (anhyd., 75 g.) was then added and the passage of HCl was continued. After 3 hours, temperature was raised to 55° which was maintained for 2 hours. Stirring and the passage of HCl were continued all the time. The mass was then left overnight, decomposed by ice, and the mixture refluxed on a water-bath for 2 hours. Benzene layer was separated out and the aqueous layer was extracted twice with benzene. The combined benzene solution was washed with water, dried over calcium chloride and the residue after removal of benzene was distilled under vacuum, b.p. 120-22°/4 mm, yield 27 g. (40%). On crystallisation from dilute alcohol, it melted at 76°. The same aldehyde was prepared by Perkin and Weizman (*loc. cit.*) using hydrocyanic acid in 32% yield.

2-Methyl-4 : 5-dimethoxycinnamic Acid (D : R′=H).—A mixture of 2-methyl-4 : 5-dimethoxybenzaldehyde (15 g.), malonic acid (15 g.), dry pyridine (30 c.c.) and piperidine (1 c.c.) was heated in anhydrous condition on a water-bath for 6 hours and then on a wire gauge for 1 hour. It was cooled and the contents were poured into a mixture of crushed ice and HCl (conc., 40 c.c.). The acid precipitated out as a yellowish solid. It crystallised from dilute alcohol in colorless needles, m.p. 153°, yield 16.5 g. (89.2%). (Found : C, 64.6 ; H, 6.1 ; OMe, 27.4. $C_{12}H_{14}O_4$ requires C, 64.9 ; H, 6.3 ; OMe, 27.5%).

β-(2-Methyl-4 : 5-dimethoxyphenyl)-propionic Acid (E : R′=H).—2-Methyl-4 : 5-dimethoxycinnamic acid was dissolved in dilute caustic soda and was reduced with sodium amalgam (500 g. of 3.5%) in the usual manner. At the end of the reaction, the liquid was acidified with HCl, when an oil separated out. On cooling and stirring, the oil solidified. It crystallised from dilute alcohol in colorless prismatic needles, m.p. 84-85°, yield 13 g. (86%). (Found : C, 64.8 ; H, 7.3. $C_{12}H_{16}O_4$ requires C, 64.3 ; H, 7.1%).

β-(2-Methyl-4 : 5-dimethoxyphenyl)-propionamide (F : R′=H).—Dry ammonia gas was passed through molten β-(2-methyl-4 : 5-dimethoxyphenyl)-propionic acid at 200° for 2 hours. The mass was then poured into water under stirring. The separated solid was filtered and washed with water. It crystallised in short colorless needles from hot water, m.p. 144-45°, yield 63%. (Found : N, 6.4. $C_{12}H_{17}O_3N$ requires N, 6.3%).

β-(2-Methyl-4 : 5-dimethoxyphenyl)-ethylamine (II : R=Me).—Finely powdered β-(2-methyl-4 : 5-dimethoxyphenyl)-propionamide (5 g.) was added to a solution of sodium hypochlorite (250 c.c. of 0.5 *N*) and stirred continually until the whole of amide dissolved completely (2 hours). The clear yellowish solution was then warmed on a water-bath for 2 hours, when a brown oil separated out. Solid KOH (30 g.) was added to

* Melting and boiling points are uncorrected.

the solution and heating continued for another hour. It was then cooled and the amine extracted out with benzene. Benzene layer was dried over solid caustic potash, benzene was removed and the residual oil was distilled, b.p. 160-62°/6 mm, yield 0.9 g. (20%). The *picrate* crystallised from dilute alcohol in yellow prismatic needles, m.p. 186°. The *hydrochloride* of the amine crystallised from ethyl acetate in colorless fine needles, m.p. 178°. (Found: C, 56.8; H, 7.7; N, 6.1. $C_{11}H_{18}O_2NCl$ requires C, 57.0; H, 7.8; N, 6.0%).

2-Ethyl 4:5-dimethoxybenzaldehyde (C: R′=Me).—A mixture of ethylveratrole (Barger and Silverschmidt, *loc. cit.*) (127 g.), zinc cyanide (127 g.) and dry benzene (400 c.c.) was subjected to Gattermann's aldehyde synthesis, modified by Adams according to a procedure described under compound (C: R′=H). The aldehyde distilled at 155-60°/9 mm, yield 65 g. (44%). The aldehyde was prepared by Barger and Silverschmidt using hydrogen cyanide.

2-Ethyl-4:5-dimethoxycinnamic acid (D: R′=Me) crystallised from dilute alcohol in colorless lustrous needles, m.p. 164-65°, yield 82%. (Found: C, 66.2; H, 6.7; OMe, 26.4. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8; OMe, 26.2%).

β-(2-Ethyl-4:5-dimethoxyphenyl)-propionic acid (E: R′=Me) was prepared by reducing 2-ethyl-4:5-dimethoxycinnamic acid with excess of sodium amalgam in the usual manner (yield 75%). It crystallised from dilute alcohol in colorless short needles, m.p. 55-56°. (Found: C, 65.2; H, 7.4. $C_{13}H_{18}O_4$ requires C, 65.5; H, 7.6%).

β-(2-Ethyl-4:5-dimethoxyphenyl)-propionamide (F: R′ = Me) crystallised in colorless short prismatic needles from hot water, m.p. 162°, yield 65%. (Found: N, 6.0. $C_{13}H_{19}O_3N$ requires N, 5.9%).

β-(2-Ethyl-4:5-dimethoxyphenyl)-ethylamine (II: R = Et).—β-(2-Ethyl-4:5-dimethoxyphenyl)-propionamide (20 g.) was treated with sodium hypochlorite solution (400 c.c. of 0.5 *N*) in the usual manner, as described under compound (II: R = Me). The amine boiled at 160-62°/3 mm, yield 4 g. (23%). *Picrate* crystallised from alcohol in light brown needles, m.p. 190-91°. Its *hydrochloride* crystallised from ethyl acetate in colorless needles, m.p. 193-94°. (Found: C, 58.3; H, 8.2; N, 5.9. $C_{12}H_{20}O_2NCl$ requires C, 58.7; H, 8.1; N, 5.7%).

3:4-Dimethoxyphenylethyl Ketone (A: R′ = Et): *Method* I.—To a solution of veratrole (75 g.) and propionyl chloride (50 g.) in dry CS_2 (300 c.c.) was added $AlCl_3$ (anhyd., 50 g.) portion-wise at ice-cold temperature. After the addition was over, the flask was maintained at this temperature for 6 hours and later on it was warmed on a water-bath for ½ hour. The contents were then poured on ice. CS_2 layer was separated out and the aqueous layer was extracted twice with fresh CS_2. From the combined carbon disulphide solution, the solvent was removed and the residue was extracted with ether. The ethereal extract was washed with dilute NaOH solution and water successively; ether was removed and the residual oil was distilled under reduced pressure, b.p. 157-60°/5 mm, yield 33 g. (31%).

Method II.—A mixture of veratrole (120 g.), propionyl chloride (100 g.), CS_2 (400 c.c.) and powdered $ZnCl_2$ (anhyd., 100 g.) was gently refluxed on a water-bath

for 4 hours, when HCl fumes continually evolved. CS_2 was distilled off, the residual mass was decomposed by boiling with water for 1 hour and the oily liquid was extracted with ether. The ether solution was washed with dilute NaOH and water successively, dried over anhydrous calcium chloride, and the residual oil after removal of ether gave on distillation the ketone (60 g., 35.7% yield); b.p. 157-59°/4 mm.

The ketone solidified on cooling and on crystallisation from alcohol yielded colorless short prisms, m.p. 58°. (Found: C, 67.9; H, 7.3. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.2%). The *semicarbazone* crystallised in colorless needles from alcohol, m.p. 193°. (Found: N, 16.8. $C_{12}H_{17}O_3N_3$ requires N, 16.7%).

1-n-*Propyl*-3:4-*dimethoxybenzene* (B:R′ = Et).—Granulated zinc (400 g.) was amalgamated with 5% mercuric chloride solution (800 c.c.) for 1 hour. This zinc was washed with water, covered with 10% HCl and allowed to boil. To the boiling solution 3:4-dimethoxyphenylethyl ketone (85 g.) was added during the course of an hour. Boiling was continued for further 6 hours and a total amount of 250 c.c. of HCl (conc.) was added at regular intervals. It was then cooled and extracted with ether. The ether solution was dried, the ether removed and the residual oil distilled in vacuum, b.p. 112-14°/4 mm, yield 52 g. (66.6%). (Found: C, 73.1; H, 9.2; OMe, 33.9. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.9; OMe, 34.4%).

2-n-*Propyl*-4:5-*dimethoxybenzaldehyde* (C:R′ = Et).—Dry HCl gas was passed through a mixture of 1-*n*-propyl-3:4-dimethoxybenzene (67 g.), zinc cyanide (50 g.) and dry benzene (250 c.c.). The mixture was stirred mechanically and after one hour $AlCl_3$ (anhyd., 40 g.) was added. Subsequent operations were the same as described under compound (C:R′ = Me). It boiled at 158-60°/4 mm, yield 20 g. (29%). Its 2:4-*dinitrophenylhydrazone* crystallised from alcohol in red needles, m.p. 185°. The *semicarbazone* crystallised from alcohol in colorless fine needles, m.p. 187°. (Found: N, 16.0. $C_{13}H_{19}O_3N_4$ requires N, 15.8%).

2-n-*Propyl*-4:5-*dimethoxycinnamic acid* (D:R′ = Et) crystallised from dilute alcohol in colorless short needles, m.p. 155°, yield 83.3%. (Found: C, 67.6; H, 7.4; OMe, 24 6. $C_{14}H_{18}O_4$ requires C, 67.2; H, 7.2; OMe, 24.8%).

β-(2-n-*Propyl*-4:5-*dimethoxyphenyl*)-*propionic acid* (E:R′ = Et) crystallised from dilute alcohol in colorless prismatic needles, m.p. 68°, yield 88%. (Found: C, 67.1; H, 7.8. $C_{14}H_{20}O_4$ requires C, 66.7; H, 7.9%).

β-(2-n-*Propyl*-4:5-*dimethoxyphenyl*)-*propionamide* (F:R′ = Et) crystallised from hot water in colorless short prisms, m.p. 110°, yield 85%. (Found: N, 5.7. $C_{14}H_{21}O_3N$ requires N, 5.57%).

β-(2-n-*Propyl*-4:5-*dimethoxyphenyl*)-*ethylamine* (II:R = *n*-Pr).—*β*-(2-*n*-Propyl-4:5-dimethoxyphenyl)-propionamide (10 g.) was treated with sodium hypochlorite solution (200 c.c. of 0.5 *N*) in the usual manner, described previously. The amine distilled at 160-62°/4 mm, yield 4.5 g. (51%). Its *picrate* crystallised from alcohol in yellow needless, m.p. 177° (decomp.).

The *amine hydrochloride* crystallised from a mixture of ethyl acetate and absolute alcohol in fine colorless needles, m.p. 235-37°. (Found: C, 57.3; H, 8.5; N, 5.7. $C_{13}H_{22}O_2NCl$ requires C, 57.9; H, 8.2; N, 5.2%)

3:4-*Dimethoxyphenyl-n-propyl Ketone* (A:R′ = *n*-Pr): *Method* I.—Veratrole (100 g.) and *n*-butyryl chloride (80 g.) in CS_2 (400 c.c.) were allowed to condense in presence of $AlCl_3$ (anhyd., 60 g.) at ice-cold temperature in a manner described in the case of compound (A:R′ = Et; method I). The ketone distilled at 160-65°/4 mm, yield 21 g. (14%).

Method II.—Veratrole (80 g.) and *n*-butyryl chloride (75 g.) in CS_2 (400 c.c.) were allowed to react in presence of $ZnCl_2$ (anhyd., 75 g.) according to the procedure described under compound (A:R′ = Et; method II). It yielded 40 g. of the ketone (36.6%). The ketone crystallised from alcohol in colorless needles, m.p. 54°. (Found: C, 69.4; H, 7.2. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.7%). The *semicarbazone* crystallised from dilute alcohol in fine colorless needles, m.p. 135°. (Found: N, 15.9; OMe, 23.4. $C_{13}H_{19}O_3N_3$ requires N, 15.8; OMe, 23.4%).

1-n-*Butyl*-3:4-*dimethoxybenzene* (B:R′ = *n*-Pr).—3:4-Dimethoxyphenyl-*n*-propyl ketone was reduced by the Clemmensen reduction as described before. It boiled at 112-15°/4 mm, yield 69%. (Found: C, 73.9; H, 9.9. $C_{12}H_{18}O_2$ requires C, 74.2; H, 9.5%).

2-n-*Butyl*-4:5 *dimethoxybenzaldehyde* (C:R′ = *n*-Pr).—To a mixture of 1-*n*-butyl-3:4-dimethoxybenzene (60 g.), zinc cyanide (75 g.), dry benzene (250 c.c.), cooled in an ice bath, was passed dry HCl. After one hour powdered $AlCl_3$ (anhyd., 40 g.) was added and the subsequent operations were conducted in a manner described before. The aldehyde distilled at 195-97°/6 mm, yield 48 g. (71%).

The 2:4-*dinitrophenylhydrazone* crystallised from alcohol in brick-red needles, m.p. 206°.

The *semicarbazone* crystallised in fine colorless needles from alcohol, m.p. 144°. (Found: N, 15.2; OMe, 22.1. $C_{14}H_{21}O_3N_3$ requires N, 15.0; OMe 22.2%).

2-n-*Butyl*-4:5-*dimethoxycinnamic acid* (D:R′ = *n*-Pr) crystallised from dilute alcohol in colorless needles, m.p. 114°, yield 95%. (Found: C, 68.4; H, 7.4. $C_{15}H_{20}O_4$ requires C, 68.2; H, 7.6%.

β-(2-n-*Butyl*-4:5-*dimethoxyphenyl*)-*propionic Acid* (E:R′ = *n*-Pr).—2-*n*-Butyl-4:5-dimethoxycinnamic acid was reduced with sodium amalgam in the usual manner. The acid crystallised from petroleum ether (b.p. 60-80°) in colorless needles, m.p. 58-59°, yield 89%. (Found: C, 67.4; H, 8.5. $C_{15}H_{22}O_4$ requires C, 67.7; H, 8.3%).

β-(2-n-*Butyl*-4:5-*dimethoxyphenyl*)-*propionamide* (F:R′ = *n*-Pr) crystallised from hot water in colorless short prisms, m.p. 105°, yield 75%. (Found: N, 5.4; OMe, 23.5. $C_{15}H_{23}O_3N$ requires N, 5.3; OMe, 23.4%).

β-(2-n-Butyl-4 : 5-dimethoxyphenyl)-ethylamine (II : R = *n*-Bu).—The above propionamide (F : R′ = *n*-Pr) (12 g.) was treated with sodium hypochlorite solution (300 c.c. of 0.5 *N*) in the usual manner, as described before. The amine distilled at 195°/10 mm, yield 2 g. (28%).

The *picrate* crystallised from alcohol in light brown needles, m.p. 152-53°. The *hydrochloride* was crystallised from absolute alcohol in colorless fine needles, m.p. 157°. (Found: C, 61.1; H, 9.1; N, 5.3. $C_{14}H_{24}O_2NCl$ requires C, 61.4; H, 8.8; N, 5.1%).

3 : 4-*Dimethoxyphenyl-n-amyl Ketone* (A : R′ = *n*-C_5H_{11}).—Veratrole (15 g.), *n*-caproyl chloride (15 g.), CS_2 (100 c.c.) and $ZnCl_2$ (anhyd., 15 g.) were worked up in the usual manner. It distilled at 150°/1 mm, yield 12 g. (49%). The ketone was a viscous liquid and did not solidify. Its *semicarbazone* was crystallised from alcohol in colorless needles, m.p. 178°. (Found: N, 14.6. $C_{15}H_{23}O_3N_3$ requires N, 14.4%).

1-n-*Hexyl-3 : 4-dimethoxybenzene* (B : R′ = *n*-C_5H_{11}).—3 : 4-Dimethoxyphenyl-*n*-amyl ketone was reduced by the Clemmensen reduction method in the usual manner. It boiled at 134-36°/2 mm, yield 77%. (Found: C, 75.8; H, 10.2. $C_{14}H_{22}O_2$ requires C, 76.7; H, 9.9%).

2-n-*Hexyl-4 : 5-dimethoxybenzaldehyde* (C : R′ = *n*-C_5H_{11}).—The aldehyde prepared in the usual manner distilled at 168-70°/2 mm, yield 30%. It did not solidify even on cooling. Its 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol in brick-red fine needles, m.p. 210°. Its *semicarbazone* crystallised from alcohol in colorless needles, m.p. 134-35°. (Found: N, 13.8. $C_{16}H_{23}O_3N_3$ requires N, 13.5%)

2-n-*Hexyl-4 : 5-dimethoxycinnamic acid* (D : R′ = *n*-C_5H_{11}) crystallised from dilute alcohol in colorless short needles, m.p. 95-96°, yield 77%. (Found: C, 70.1; H, 8.3. $C_{17}H_{24}O_4$ requires C, 69.8; H, 8.2%).

β-(2-n-Hexyl-4 : 5-dimethoxyphenyl)-propionic Acid (E : R′ = *n*-C_5H_{11}).—2-*n*-Hexyl-4 : 5-dimethoxycinnamic acid was reduced by sodium amalgam in the usual manner. It crystallised in colorless microneedles from dilute alcohol, m.p. 70-72°, yield 94%. (Found: C, 69.1; H, 9.1. $C_{17}H_{26}O_4$ requires C, 69.4; H, 8.8%).

β-(2-n-Hexyl-4 : 5-dimethoxyphenyl)-propionamide (F : R′ = *n*-C_5H_{11}).—The amide on twice crystallisation from dilute alcohol appeared in colorless short needles m.p. 58-60°, yield 60%. (Found: N, 4.6. $C_{17}H_{27}O_3N$ requires N, 4.8%).

β-(2-n-Hexyl-4 : 5-dimethoxyphenyl)-ethylamine (II : R = *n*-C_6H_{13}).—*β-(2-n*-Hexyl-4 : 5-dimethoxyphenyl)-propionamide (5 g.) was dissolved in dry methanol (10 c.c.). This was added to a solution of sodium methoxide prepared out of sodium (0.8 g.) and methanol (30 c.c.). To the cold solution bromine (2.6 g.) was added and the mixture was heated on a water-bath for ½ hour. The solution was made just acidic with acetic acid and methanol was removed by distillation. The residual mass was then hydrolysed with NaOH solution (25%). It was then extracted with benzene and the benzene solution was twice extracted with (dilute) HCl. The combined acid

solution was made alkaline with NaOH solution and the separated amine was extracted with ether. The ethereal solution was dried over solid caustic potash, and on addition of a saturated solution of dry hydrogen chloride in ether, to the ethereal solution of the amine, hydrochloride of the amine separated out, yield 1.5 g. (30%). It crystallised from absolute alcohol in colorless needles, m.p. 123-24°. (Found: C, 63.8; H, 9.4; N, 4.7. $C_{16}H_{28}O_2NCl$ requires C, 63.7; H, 9.3; N, 4.6%). Its *picrate* crystallised from dilute alcohol in light brown needles, m.p. 162-63°.

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CITRATE COMPLEX OF NICKEL

By Rabindra Kumar Patnaik and S. Pani

Citrate complex of nickel has been investigated by p_H titration method within the p_H range 2.5 to 7. A neutral complex C is formed at lower p_H due to the reaction of a nickel ion and citric acid with the simultaneous liberation of two protons. The equilibrium constant of this reaction has been found to be 7.97×10^{-5}. This complex with increase in p_H dissociates to a H^+ ion and complex C_1^-, the dissociation constant being 1.75×10^{-4}. At still higher p_H the complex C_1^- further dissociates like a monobasic acid to C_2^{2-} and H^+. The dissociation constant of the latter reaction is 2.35×10^{-8}. The structures of these complexes have been discussed.

Citrate complex of nickel has been studied by Bobbtelsky and Jorean (*J. Amer. Chem. Soc.*, 1945, **67**, 1824) and the existence of a complex containing one citrate ligand per atom of nickel has been reported. The investigation was done in the higher p_H region. The nature of the complex, if any, existing in the lower p_H region appears not to have been investigated. It was therefore thought worthwhile to investigate the problem more thoroughly.

Experimental

The chemicals used were of Analar quality. In the three p_H titrations described below, p_H was measured by a Marconi p_H-meter. Each experiment consists of two p_H titrations and the results are graphically represented by the curve (A) and (B) respectively in Figs. 1-3. Curve (B) represents results obtained with the solution containing a known amount of nickel sulphate, whereas curve (A) represents results obtained in identical condition with the solution containing no nickel sulphate. The details of the experiment are recorded below.

Experiment (I) (Fig. 1).—Curve (A) represents the results of p_H titration of 55 c.c. of a solution containing 0.003 g. mol. of citric acid, and curve (B) that of the same volume of the solution containing 0.003 g. mol. of citric acid and 0.0025 g. mol. of nickel sulphate against *N*-NaOH at 32.5°.

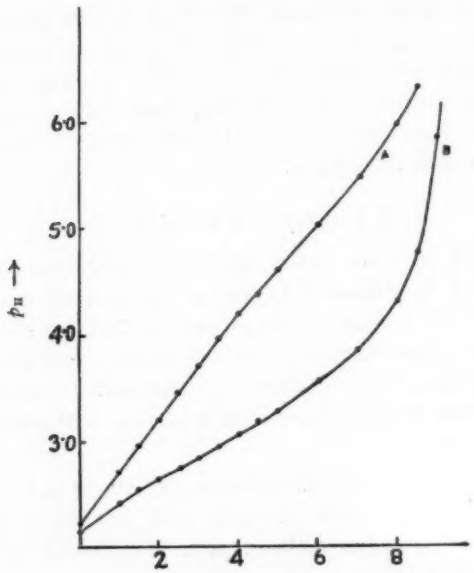
Experiment (II) (Fig. 2).—Curve (A) represents the results obtained by titrating 100 c.c. of a solution containing 0.025 g. mol. of potassium nitrate and curve (B) that of the same volume of the solution containing 0.025 g. mol. of nitrate and 0.001 g. mol. of nickel sulphate against 2/3 neutralised citric acid solution of concentration 0.1*M* at 32°. Potassium nitrate was added to maintain the ionic strength of both the systems very nearly the same.

Experiment (III) (Fig. 3).—Curve (A) represents the results obtained by titrating 100 c.c. of a solution containing 0.025 g. mol. of potassium nitrate, and (B) that of the same volume of the solution containing 0.025 g. mol. of patassium nitrate and 0.00125 g. mol. of nickel sulphate against 0.1*M* sodium citrate solution at 32.5°

Discussion

The p_H of the system (B) in each case is lower than the corresponding p_H in the system (A). Acid is therefore liberated due to the reaction of nickel ion with citrate ligand and formation of a complex. In Experiment (I : Fig. 1) the horizontal distance between the two curves is the measure of the amount of acid liberated due to the formation of a complex. The horizontal distance at first increases with increasing p_H and then decreases ; at about p_H 6, the two curves are very close and the horizontal distance is negligible. This shows that at lower p_H some of the undissociated carboxyl groups of citric acid are induced to ionise due to the formation of a complex with nickel, before the actual p_H for the ionisation of these carboxyl groups is reached. Citric acid in presence of nickel behaves comparatively as a strong tribasic acid.

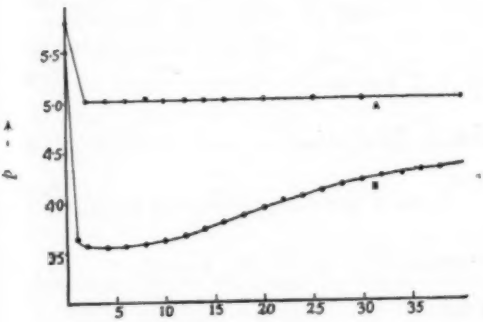
Fig. 1



No proton is liberated from the hydroxyl group of the citrate ligand due to the formation of the complex, as in such a case citric acid would behave as a tetrabasic acid (in presence of nickel). In Experiment (II : Fig. 2) the p_H of the system containing no nickel is very nearly constant, even with different amounts of two third neutralised citric acid ($HCit^{2-}$ ions). The p_H is, however, low in presence of nickel. This is not due to simple removal of $HCit^{2-}$ ions from the solution by nickel, as this would not change the p_H. This is probably due to the formation of a complex which is a stronger acid than $HCit^{2-}$. In Experiment (III : Fig. 3) the p_H of the system containing nickel is lower than that of the other system. This is probably due to the removal of citrate ion from the solution by nickel ion. The added citrate ion is

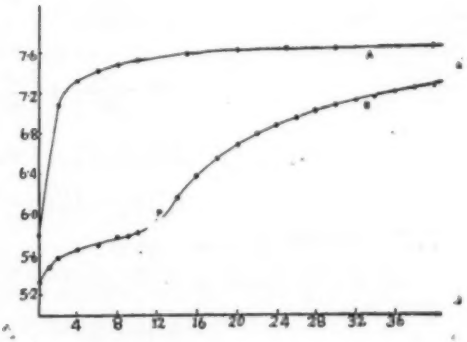
most probably completely removed from the solution and, hence, the p_H does not rise. This complete removal of citrate ion by nickel and formation of an 1 : 1 complex are indicated by the inflection at about P in curve (B) in Fig 3. The p_H should have

FIG. 2



Na_2H-*citrate in c.c.*

FIG. 3



Na-*citrate in c.c.*

increased rapidly after the inflection if no other reaction would have taken place ; but the rise in p_H is very gradual. The 1 : 1 complex formed by the interaction of citrate ligand with nickel is probably an acid and dissociates with increasing p_H.

Calculation of Equilibrium Constant

The reaction taking place in Experiment (I) may be represented by

$$Ni^{2+} + H_3Cit \rightleftharpoons C + n\,H^+ \quad \ldots \quad \ldots \quad (1)$$

where C is the nickel citrate complex. The charge of the complex is not shown. The equilibrium constant is given by the equation (1-1) where $[Ni^{2+}]$, $[H_3Cit]$, [C] and $[H^+]$ represent the molar concentration of nickel ion, citric acid, the complex and hydrogen ion respectively.

$$\frac{[C] \times [H^+]^n}{[Ni^{2+}][H_3Cit]} = K \quad \ldots \quad \ldots \quad (1\text{-}1)$$

Let A and B be two points on the same p_H axis on curve (A) and (B) respectively in Fig. 1. The reaction taking place at A is the neutralisation of citric acid and formation of dihydrogen citrate ion, monohydrogen citrate ion and citrate ion. At B the complex C is formed besides the neutralisation of citric acid. The molar concentrations of the ions and molecules at A are represented by $[\ ]_A$ and that at B by $[\ ]_B$. The p_H being the same, the concentration of the hydrogen ion is represented by $[H^+]$. k_1, k_2 and k_3 are respectively the first, the second and the third dissociation constant of citric acid ($k_1 = 8.32 \times 10^{-4}$; $k_2 = 4.07 \times 10^{-5}$ and $k_3 = 3.24 \times 10^{-6}$; Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 1949, **32**, 1682). It can be shown

that

$$\frac{\Delta[\mathrm{NaOH}] - \frac{a}{b}\Delta[\mathrm{Ct}]}{[\mathrm{C}]} = n + \frac{a}{b} \quad \ldots \quad \ldots \quad (2)$$

where,

$$a = \frac{k_1}{[\mathrm{H}^+]} + 2\frac{k_1 \times k_2}{[\mathrm{H}^+]^2} + 3\frac{k_1 \times k_2 \times k_3}{[\mathrm{H}^+]^3} \quad \ldots \quad \ldots \quad (2\text{-}1)$$

$$b = \frac{k_1}{[\mathrm{H}^+]} + \frac{k_1 \times k_2}{[\mathrm{H}^+]^2} + \frac{k_1 \times k_2 \times k_3}{[\mathrm{H}^+]^3} + 1 \quad \ldots \quad \ldots \quad (2\text{-}2)$$

$$\Delta[\mathrm{NaOH}] = [\mathrm{NaOH}]_B - [\mathrm{NaOH}]_A \quad \ldots \quad \ldots \quad (2\text{-}3)$$

$$\Delta[\mathrm{Ct}] = [\mathrm{Ct}]_B - [\mathrm{Ct}]_A \quad \ldots \quad \ldots \quad \ldots \quad (2\text{-}4)$$

[Ct] represents the total citrate.

When the formation of the complex is complete [C] = [$NiSO_4$] Hence,

$$\frac{\Delta[\mathrm{NaOH}] - \frac{a}{b}\Delta[\mathrm{Ct}]}{[\mathrm{NiSO_4}]} = n + \frac{a}{b} \quad \ldots \quad \ldots \quad (3)$$

[H^+] is obtained from the curve. $[Ct]_A$, $[NaOH]_A$, $[Ct]_B$, $[NaOH]_B$ and [$NiSO_4$] are obtained from the g. mol. of the substance taken or added and the corresponding total volume of the solution (total volume = initial volume + volume of alkali added at A or B). Δ[NaOH] and Δ[Ct] are calculated, and substituting in equation (3), the value of n is obtained. The value thus calcu'ated are shown in Table I.

TABLE I

p_H.	a/b.	$\Delta[NaOH]\times 10^2$.	$\Delta[Ct]\times 10^3$.	$[NiSO_4]\times 10^2$.	n.	$[C]\times 10^2$.	$[H_3Cit]\times 10^2$.	$[Ni^{2+}]\times 10^2$.	$K\times 10^5$.
2.50	0 2131	1.581	0.86	4 432	1.014	0.895	3 492	3.537	7.24
2 60	0.2561	2.082	1.14	4 393	1 090	1.211	3 040	3.182	7.90
2.70	0.3046	2.404	1 32	4 362	1.127	1.442	2.660	2.920	7.39
2 75	0 3311	2.553	1.39	4.340	1.146	1.156	2.468	2 783	7 17
2.80	0.3589	2.710	1 48	4.325	1.170	1 684	2.278	2.641	7 03
2.90	0 4184	3.177	1.74	4.287	1.261	2.053	1.839	2.234	7 92
3.00	0 4826	3.636	2 00	4.251	1.376	2.460	1.417	1.791	0.69
3.10	0.5499	3.767	2 06	4.230	1.430	2.674	1.144	1 556	9.48
3 50	0 8351	5.025	2.74	4 111	2 057	...	...	...	...
3.60	0.9080	5.285	2.89	4.084	2.202	...	...	...	...
3.70	0.9802	5.538	3.02	4 058	2.345	...	...	...	...
3 75	1.016	5.665	3 09	4.044	2 417	...	...	...	...
3.80	1.055	5 642	3.08	4.038	2.450	...	...	...	...
3.90	1.128	5.748	3.15	4.019	2.558	...	...	...	...
4.00	1.203	5.856	3.20	3.999	2.667	...	...	...	...
4.10	1.281	5.817	3.17	3 987	2.740	...	...	...	...
4.20	1 362	5.781	3.16	3.974	2.817	...	...	...	...
4.30	1.445	5.606	3.05	3.968	2.858	...	...	...	...

The value of n is never less than 1. n is < 2 below and > 2 above p_H 3.5. The value of n being < 2, it is evident that the formation of the complex C is not complete below p_H 3.5. [C] is calculated at $p_H < 3.5$ by equation (2), assuming the value of n to be 2. The concentration of nickel ion is obtained by subtracting [C] from [$NiSO_4$]. K is calculated by equation (1-1). The values are shown in Table I in the last column. The mean value of K is 7.97×10^{-5}.

Towards the higher p_H range ($n > 2$) more than two protons are liberated. The formation of the complex C is complete and it dissociates like an acid with increasing p_H.

$$C \rightleftharpoons C_1^- + H^+ \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

$$\frac{[C_1^-] \times [H^+]}{[C]} = K_1 \quad \ldots \quad \ldots \quad \ldots \quad (4\text{-}1)$$

The sum of the concentrations of C and C_1^- would be equal to total nickel.

$$[C] + [C_1^-] = [NiSO_4] \quad \ldots \quad \ldots \quad \ldots \quad (4\text{-}2)$$

Due to the formation C and C_1^- respectively two and three protons would be liberated.

Total acid liberated due to the formation of complex $= 2[C] + 3[C_1^-]$. Hence,

$$\frac{2[C] + 3[C_1^-]}{[NiSO_4]} = n \quad \ldots \quad \ldots \quad \ldots \quad (4\text{-}3)$$

or

$$\frac{[C_1^-]}{[NiSO_4]} = n - 2 \quad \ldots \quad \ldots \quad \ldots \quad (4\text{-}4)$$

and

$$\frac{[C]}{[NiSO_4]} = 3 - n \quad \ldots \quad \ldots \quad \ldots \quad (4\text{-}5)$$

The value of K_1 can be calculated by substituting $[C_1^-]/[NiSO_4]$ and $[C]/[NiSO_4]$ in place of the exact value of $[C_1^-]$ and [C] respectively. The values are recorded in Table II below. The mean value of K_1 is 1.75×10^{-4}.

TABLE II

p_H.	$[C_1^-]/[NiSO_4]$.	$[C]/[NiSO_4]$.	$K_1 \times 10^4$.
3.70	0.3480	0.6520	1.05
3.75	0.4170	0.5830	1.27
3.80	0.4500	0.5500	1.29
3.90	0.5580	0.4420	1.59
4.00	0.6670	0.3330	2.00
4.10	0.7400	0.2600	2.26
4.20	0.8170	0.1830	2.82

In Experiment (II) increasing amount of 2/3 neutralised acid is added to a definite amount of nickel sulphate. It is assumed that 2/3 neutralised citric acid mostly consists of $HCit^{2-}$ ion. These ions react with nickel ion affording the complex C.

$$Ni^{2+} + HCit^{2-} \rightleftharpoons C \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

$$\frac{[C]}{[Ni^{2+}] \times [HCit^{2-}]} = K_2 \quad \ldots \quad \ldots \quad \ldots \quad (5\text{-}1)$$

The complex C being a stronger acid than $HCit^{2-}$ (dissociation constant of C is 1.75×10^{-4} and that of $HCit^{2-}$ is 3.24×10^{-6}) dissociates according to the reaction (4). As sufficient $HCit^{2-}$ is introduced, the formation of the complex C is complete and dissociation of C to C_1^- and H^+ continues with increasing addition of 2/3 neutralised citric acid. The equilibrium constants K_1 and K_2 can be calculated from the results of Experiment (II). K_2 differs form K (the equilibrium constant of the reaction of formation of C from nickel ion and citric acid) by a constant and it can be shown that

$$\frac{K}{k_1 \times k_2} = K_2 \qquad \ldots \qquad \ldots \qquad \ldots \quad (5\text{-}2)$$

The results obtained from this experiment would be more reliable since the ionic strength is very nearly constant and would be a confirmation of the results obtained before.

In the previous experiment with 20% citrate in excess to total nickel, the formation of the complex C is complete at about p_{Ni} 3.5. The p_{Ni} in this system (curve B, Fig. 2) is always above 3.5. Hence, it is expected that after addition of 20% citrate in excess to the amount of nickel in the solution, the formation of the complex C would be complete. Some nickel ion will be present when the proportion of nickel to citrate in the solution > 1.

$$\text{Total nickel} = [NiSO_4] = [C] + [C_1^-] + [Ni^{2+}] \qquad \ldots \qquad \ldots \quad (6)$$

When the formation of the complex is complete $[Ni^{2+}]$ is very small and

$$[NiSO_4] = [C] + [C_1^-] \qquad \ldots \qquad \ldots \quad (6\text{-}1)$$

Total citrate $= [Ct] = [C] + [C_1^-] + [H_3Cit] + [H_2Cit^-] + [HCit^{2-}] + [Cit^{3-}]$. The concentration of citric acid would be small and may be neglected. Hence

$$[Ct] = [C] + [C_1^-] + [HCit^{2-}] \times \left(\frac{[H^+]}{k_2} + 1 + \frac{k_2}{[H^+]} \right)$$

or

$$[Ct] = [C] + [C_1^-] + a\,[HCit^{2-}] \qquad \ldots \qquad \ldots \quad (6\text{-}2)$$

The citrate added to the system is two thirds neutralised (*i. e*, 2 g. mol. NaOH per g. mol. of citric acid has been added). The amount of acid liberated due to the formation of the complex would be equal to $[C_1^-]$ which would react with some citrate or monohydrogen citrate ion. If one considers from pure citric acid,

Total acid liberated $= 2[C] + 3[C_1^-] + [H_2Cit^-] + 2[HCit^{2-}] + 3[Cit^{3-}]$

Acid neutralised $= 2[Ct]$.

Hence

$$2[Ct] + [H^+] = 2[C] + 3[C_1^-] + [HCit^{2-}] \times \left(\frac{[H^+]}{k_2} + 2 + 3\,\frac{k_2}{[H^+]} \right)$$

or

$$2[Ct] + [H^+] = 2[C] + 3[C_1^-] + b[HCit^{2-}] \qquad \ldots \qquad \ldots \quad (6\text{-}3)$$

When the formation of C is complete, the equation (6-2) reduces to

$$[Ct] = [NiSO_4] + a\,[HCit^{2-}]$$

or

$$[HCit^{2-}] = \frac{[Ct] - [NiSO_4]}{a} \qquad \ldots \qquad \ldots \qquad \ldots \quad (6\text{-}4)$$

Substituting the value of $[HCit^{2-}]$ in equation (6-3) and taking $[C] + [C_1^-] = [NiSO_4]$ one gets

$$2[Ct] + [H^+] = 2[NiSO_4] + [C_1^-] + \frac{b}{a}([Ct] - [NiSO_4])$$

or $$[Ct] \times \left(2 - \frac{b}{a}\right) + [H^+] - [NiSO_4] \times \left(2 - \frac{b}{a}\right) = [C_1^-]$$

or $$([Ct] - [NiSO_4]) \times \left(2 - \frac{b}{a}\right) + [H^+] = [C_1^-] \quad \ldots \quad (6\text{-}5)$$

$[H^+]$ is obtained from curve (B) in Fig. 2, and a and b are calculated. $[Ct]$ or $[NiSO_4]$ is obtained from the g. mol. of two thirds neutralised citric acid added or the g. mol. of nickel sulphate taken and the total volume of the solution. $[C]$ is obtained by subtracting $[C_1^-]$ from $[NiSO_4]$ and K_1 is calculated by equation (4-1). The values are shown in Table III. The mean value 1.945×10^{-4} is in good agreement with the value previously calculated from Experiment (I).

TABLE III

p_H.	b/a.	$[NiSO_4] \times 10^3$.	$[Ct] \times 10^3$.	$[C_1^-] \times 10^3$.	$[C] \times 10^3$.	$K_1 \times 10^4$.
3.75	1.192	8.740	1.259	3.289	5 451	1.07
3.80	1.212	8.620	1.379	4.232	4.388	1.53
3.85	1.233	8.517	1.482	4.973	3.544	1.98
3.90	1.255	8.405	1.597	5.758	2.647	2.74
3.95	1.279	8.307	1.694	6 334	1.973	3.60

The mean value of $K_1 = 1.94 \times 10^{-4}$.

For the range in which proportion of nickel to citrate is ≥ 1, the calculation can be made as follows:

$$[C] = \frac{[H^+]}{K_1}[C_1^-].$$

Substituting the value of $[C]$ in equation (6-2) and (6-3), one gets

$$[Ct] = [C_1^-] \times \left(1 + \frac{[H^+]}{K_1}\right) + a\,[HCit^{2-}] \quad \ldots \quad \ldots \quad (7)$$

and

$$2[Ct] + [H^+] = [C_1^-] \times \left(3 + 2\frac{[H^+]}{K_1}\right) + b\,[HCit^{2-}] \ldots \quad (7\text{-}1)$$

Substituting the value of $[HCit^{2-}]$ from equation (7), the equation (7-1) reduces to

$$2[Ct] + [H^+] = [C_1^-] \times \left(3 + \frac{2[H^+]}{K_1}\right) + \frac{b}{a}\left\{[Ct] - [C_1^-] \times \left(1 + \frac{[H^+]}{K_1}\right)\right\}$$

$$\text{or} \quad \frac{[Ct] \times \left(2 - \frac{b}{a}\right) + [H^+]}{\left(3 - \frac{b}{a}\right) + \frac{[H^+]}{K_1}\left(2 - \frac{b}{a}\right)} = [C_1^-] \quad \ldots \quad \ldots \quad \ldots \quad (7\text{-}2)$$

All the quantities in equation (7-2) except $[C_1^-]$ are known. $[C_1^-]$ is calculated at different p_H values and C by equation (4-1), substituting the values of $[C_1^-]$ and K_1. $[N_1^{2+}]$ is obtained by subtracting the sum of the concentrations of C and C_1^- from $[NiSO_4]$. $[HCit^{2-}]$ is calculated from equation (7-1). The values of K_2, thus calculated, are shown in Table IV. The values are fairly constant.

TABLE IV

p_H.	b/a.	$[Ct] \times 10^3$.	$[NiSO_4] \times 10^3$.	$[C_1^-] \times 10^3$.	$[C] \times 10^3$.	$[HCit^{2-}] \times 10^4$.	$[Ni^{2+}] \times 10^3$.	$K_2 \times 10^{-3}$	$K \times 10^5$.
3.64	1.155	0.9902	9.902	0.3753	0.4421	0.2594	9.085	1.876	6.352
3.58	1.137	1.961	9.804	0.6452	0.8726	0.5929	8.285	1.776	6.015
3.56	1.132	2.913	9.709	0.9374	1.327	0.7202	7.447	2.475	8.379
3.57	1.134	5.661	9.434	1.688	2.335	2.150	5.411	2.007	6.797
3.58	1.137	6.542	9.346	1.950	2.637	2.612	4.759	2.121	7.185
3.59	1.140	7.408	9.260	2.210	2.920	3.113	4.130	2.272	7.691
3.62	1.145	8.256	9.175	2.509	3.095	3.832	3.571	2.261	7.658
3.63	1.152	9.090	9.090	2.745	3.309	4.550	3.036	2.395	8.110

The values of K, calculated from the corresponding values of K_2 according to the equation (5-2) are in agreement with those calculated from the results of Experiment (I). The mean value is 7.53×10^{-5}.

In Experiment (III) (Fig. 3) the complex C_1^- is formed with increasing addition of sodium citrate as the p_H is high. The complex is a very stable one and the formation is very nearly complete when 1 g. mol. of sodium citrate is added per g. atom of nickel. On further addition of sodium citrate, the p_H, as expected, does not rise rapidly. It is very probable that complex C_1^- dissociates like a monobasic acid as the p_H is increased by increasing addition of sodium citrate. The reaction may be represented by equation (8). The proton thus liberated, is partly consumed by the citrate ion.

$$C_1^- \rightleftharpoons C_2^{2-} + H^+ \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

$$\frac{[C_2^{2-}] \times [H^+]}{[C_1^-]} = K_3 \quad \ldots \quad \ldots \quad \ldots \quad (8\text{-}1)$$

Total citrate = [Ct] = free citrate + citrate in the complex.

Free citrate = $[Ct^{3-}] + [HCit^{2-}] + [H_2Cit^-] + [H_3Cit]$.

The concentration of citric acid would be small and may be neglected. Hence

$$\text{Free citrate} = [HCit^{2-}] \times \left(\frac{k_3}{[H^+]} + 1 + \frac{[H^+]}{k_2} \right) = a\,[HCit^{2-}] \quad \ldots \quad (9)$$

Citrate in the complex = $[C_1^-] + [C_2^{2-}] = [NiSO_4]$ ... ... (9-1)

Hence

$$[Ct] - [NiSO_4] = a\,[HCit^{2-}] \quad \ldots \quad \ldots \quad \ldots \quad (9\text{-}2)$$

The amount of acid liberated = $[C_2^{2-}]$.

The amount of acid consumed = $[HCit^{2-}] + 2[H_2Cit^-]$

$$= [HCit^{2-}] \times \left(1 + 2\,\frac{[H^+]}{k_2} \right) = b\,[HCit^{2-}].$$

Hence

$$[C_2^{2-}] = [H^+] + b\,[HCit^{2-}] \quad \ldots \quad \ldots \quad \ldots \quad (9\text{-}3)$$

Substituting the value of $[HCit^{2-}]$ from equation (9-2), the above equation is reduced to

$$[C_2^{2-}] = [H^+] + \frac{b}{a}\,([Ct] - [NiSO_4]) \quad \ldots \quad \ldots \quad (9\text{-}4)$$

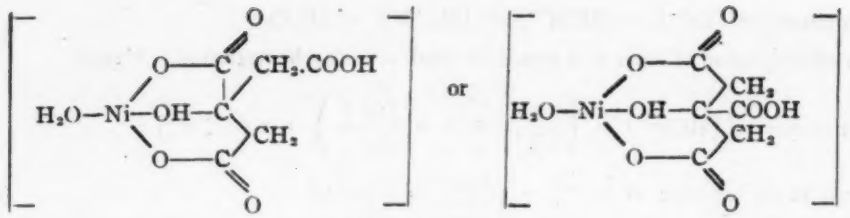
$[H^+]$ is obtained from curve (B) in Fig. 3 and a, b, $[Ct]$ and $[NiSO_4]$ are calculated as before. $[C_2^{2-}]$ is calculated by equation (9-4). $[C_1^-]$ is obtained by subtracting $[C_2^{2-}]$ from $[NiSO_4]$. K_3 is calculated by equation (8-1). The results are recorded in Table V. The mean value of K_3 is 1.35×10^{-8}.

TABLE V

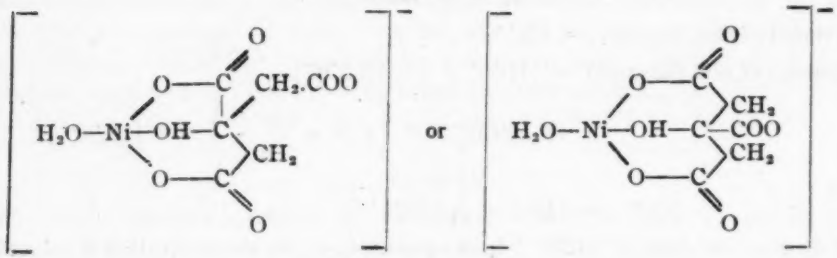
p_H.	$[NiSO_4]$.	$[Ct]$.	b/a.	$[C_2^{2-}] \times 10^4$.	$[C_1^-] \times 10^2$.	$K_3 \times 10^8$.
6.2	0.01092	0.01259	0.1676	2.799	1.064	1.660
6.3	0.01085	0.01319	0.1371	3.207	1.053	1.530
6.4	0.01074	0.01409	0.1115	3.736	1.037	1.430
6.5	0.01064	0.01482	0.0903	3.775	1.026	1.160
6.6	0.01052	0.01582	0.0728	3.857	1.024	0.955

Structure of the Complex

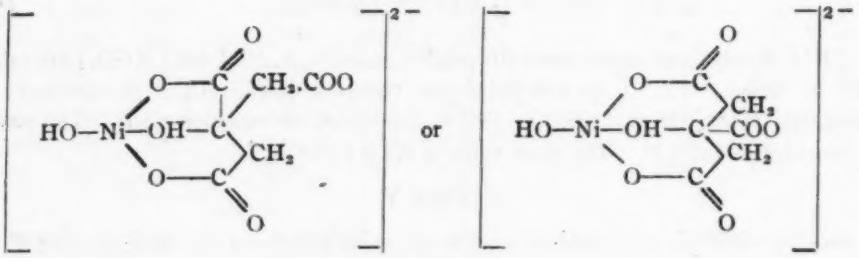
In the Experiment (I) it is observed that n is never <1. In the formation of the complex C two of the three carboxyl groups of citric acid are attached. It is, however, difficult to predict which of the two carboxyl groups take part in the reaction. For the formation of a stable complex, the formation of five- or six-membered ring is necessary. Hence, the hydroxyl group of citric acid most probably forms a co-ordinate bond with nickel. The complex is expected to be a four co-ordination one. Since the citrate ligand can occupy only three co-ordination position, the fourth co-ordination position is occupied by a molecule of water. There is, however, certain justification in assuming this. The complex is an aquo-complex, the water molecule of which ionises at about neutral point furnishing the hydroxo-complex. The structures may be represented as follows:



(Complex C)

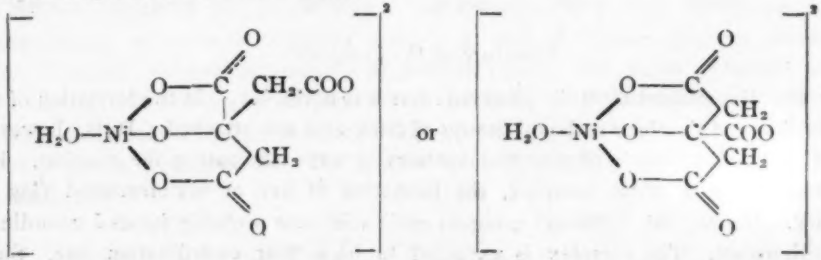


[Complex C_1^-].



[Complex C_2^{2-}].

If the proton is liberated from the hydroxyl group joined to the nickel atom in complex C but not from water molecule as suggested above, the complex C may be represented by structures shown below.



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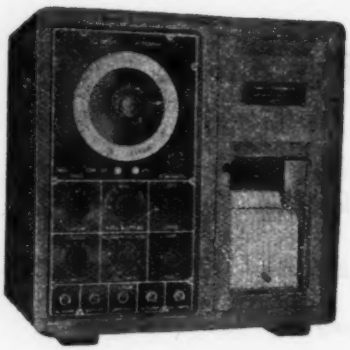

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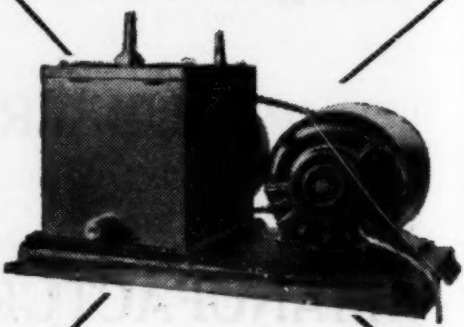

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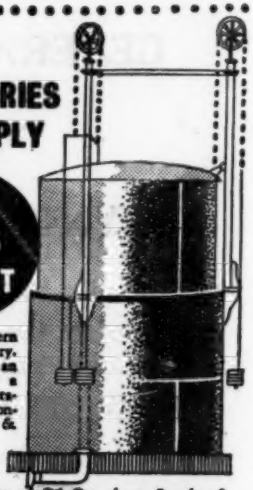

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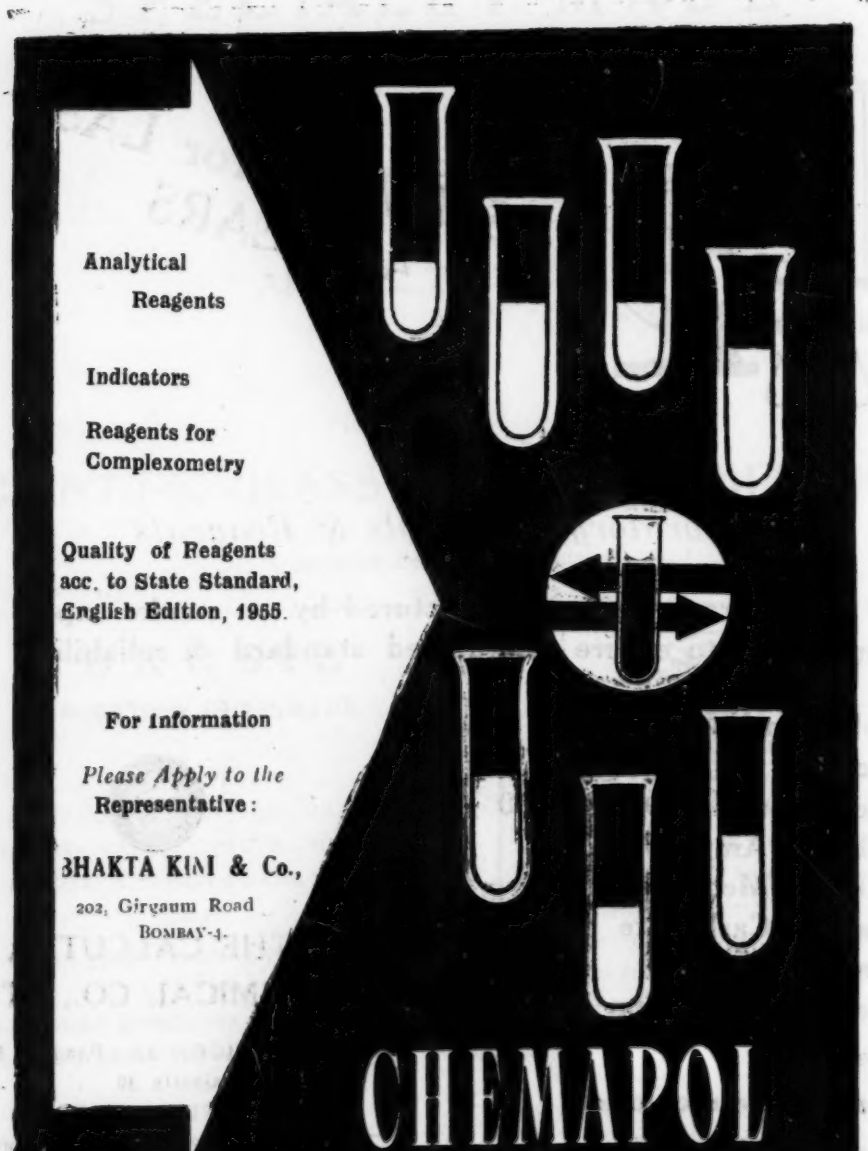

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